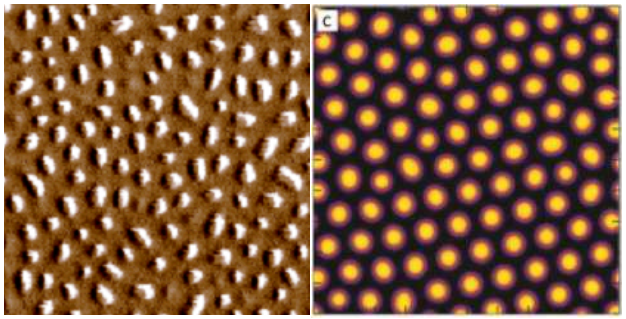
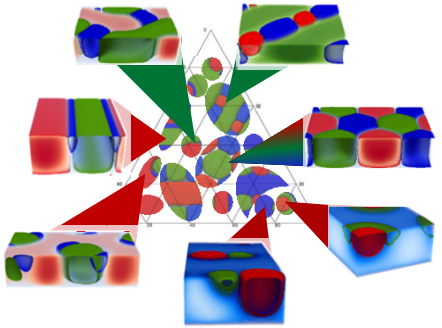
SAND2017-11175PE





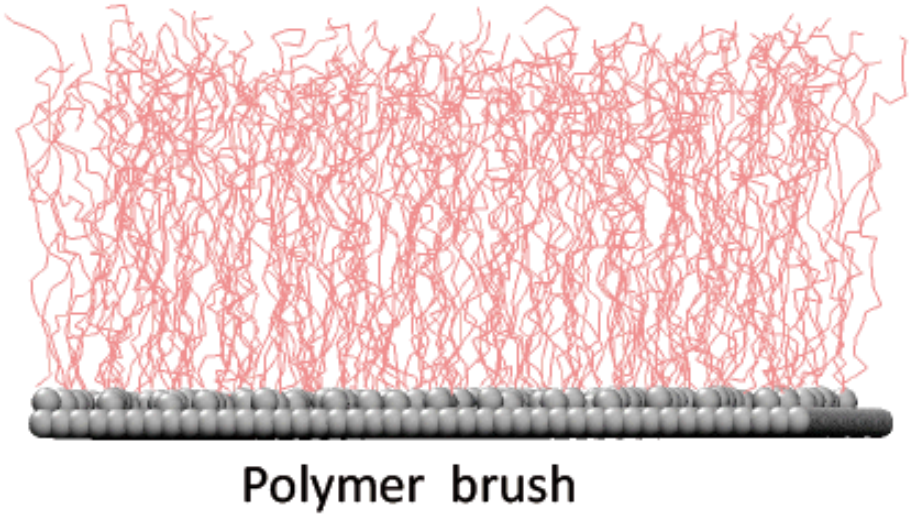
Pattern Formation and Particle Assembly with Mixed Polymer Brushes

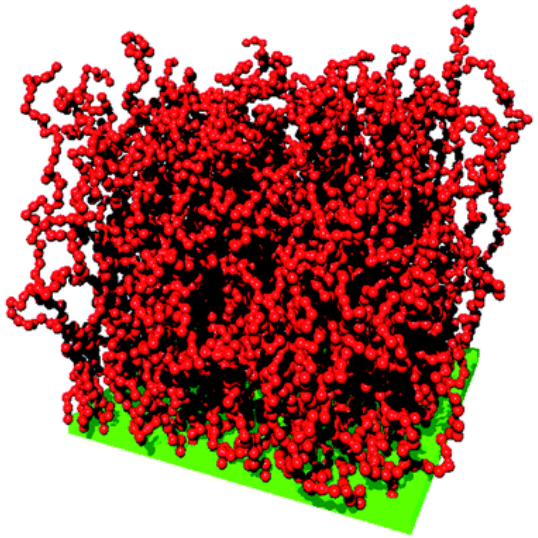
Amalie L. Frischknecht

Sandia National Laboratories is a multimission laboratory managed and operated by National Technology and Engineering Solutions of Sandia LLC, a wholly owned subsidiary of Honeywell International Inc. for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.

What is a polymer brush?

polymer chains covalently bonded to a surface

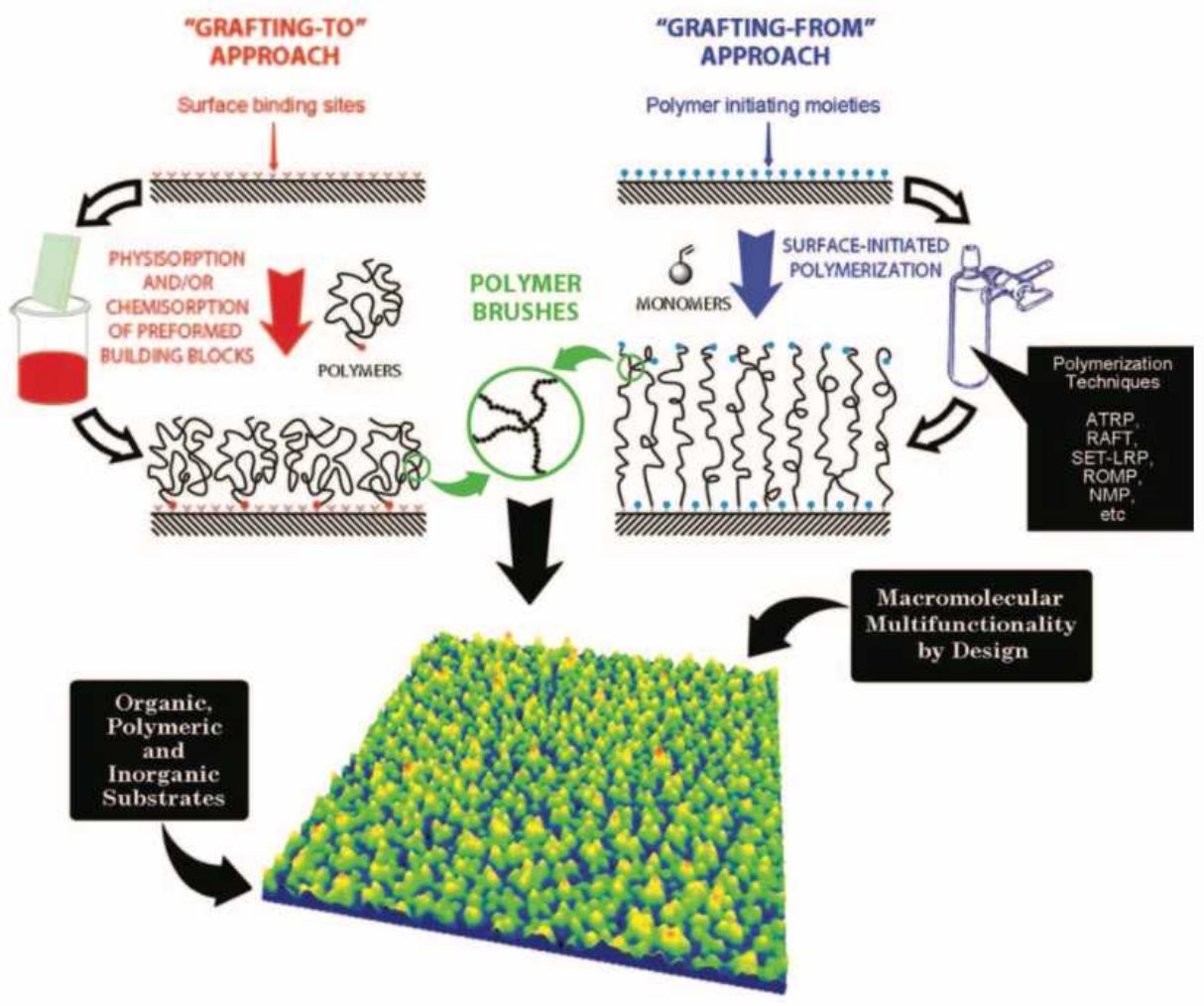




http://erbas.web.unc.edu

A. Milchev and K. Binder, Soft Matter **10**, 3783 (2014).

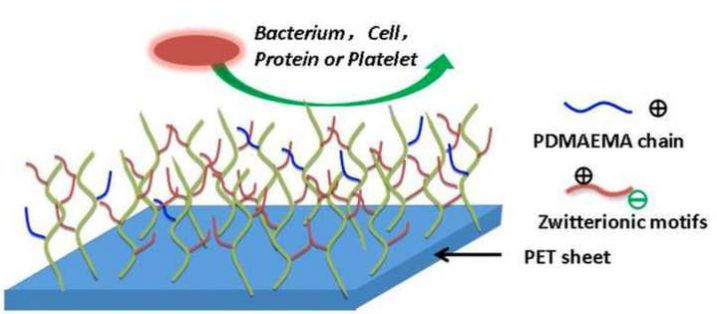
How to make polymer brushes



O. Azzaroni, J Polym Sci Pol Chem **50**, 3225 (2012).

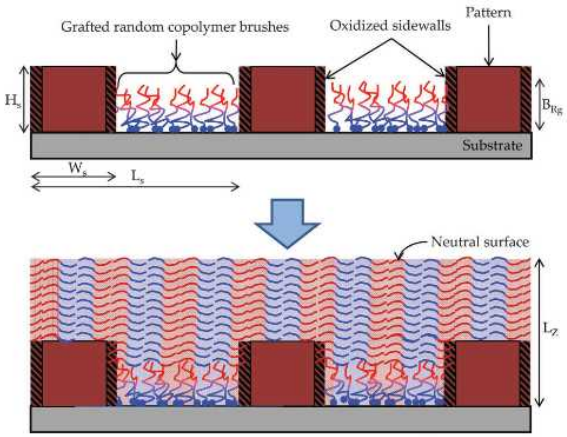
Applications of polymer brushes

antifouling surfaces



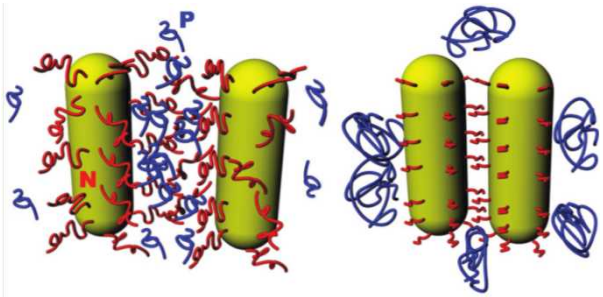
X. Jin, J. Yuan, and J. Shen, Colloids and Surfaces B: Biointerfaces **145**, 275 (2016).

block copolymer assembly

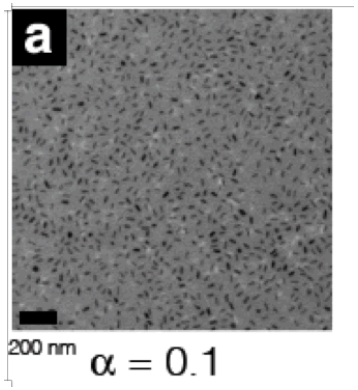


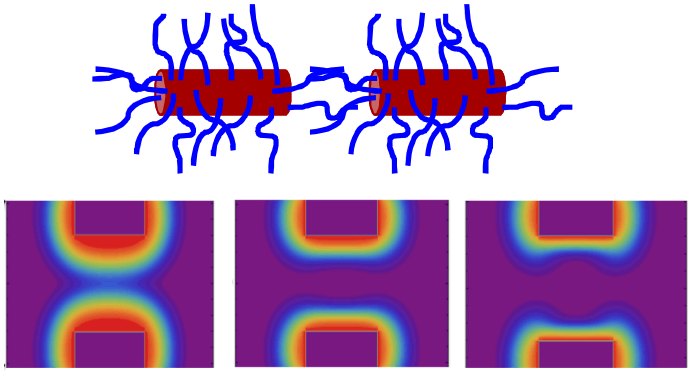
G. Pandav, W.J. Durand, C.J. Ellison, C.G. Willson, and V. Ganesan, Soft Matter **11**, 9107 (2015).

controlling particle stability



M.J.A. Hore, A.L. Frischknecht, and R.J. Composto, ACS Macro Lett. **1**, 115 (2012).



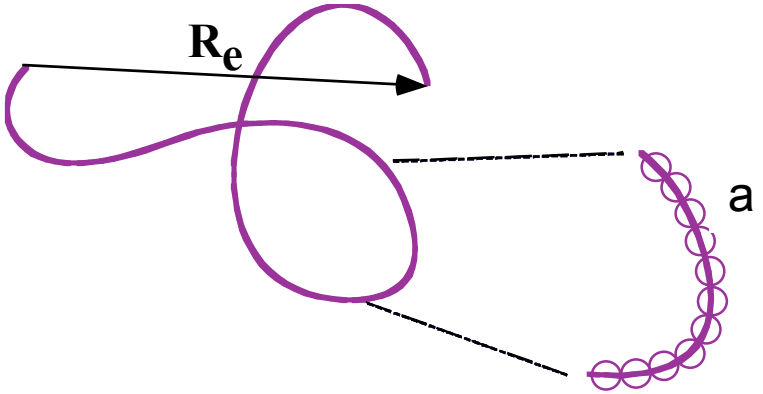


C.L. Ting, R.J. Composto, and A.L. Frischknecht, Macromolecules **49**, 1111 (2016).

Structure of polymer brushes

free polymers are random walks

$$R_e \sim N^{1/2}$$

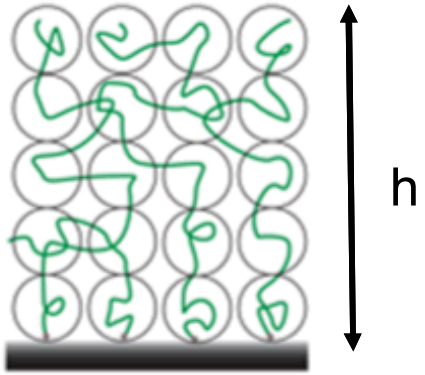


brush: put σ chains/unit area

if close enough in a brush, polymers must stretch:

$$F = k_B T \left[\frac{3h^2}{2Na^2} + \frac{wN^2\sigma}{h} \right]$$

stretching entropy interactions



minimize free energy:

$$h \sim N(\sigma w)^{1/3}$$

Structure of polymer brushes

free polymers are random walks

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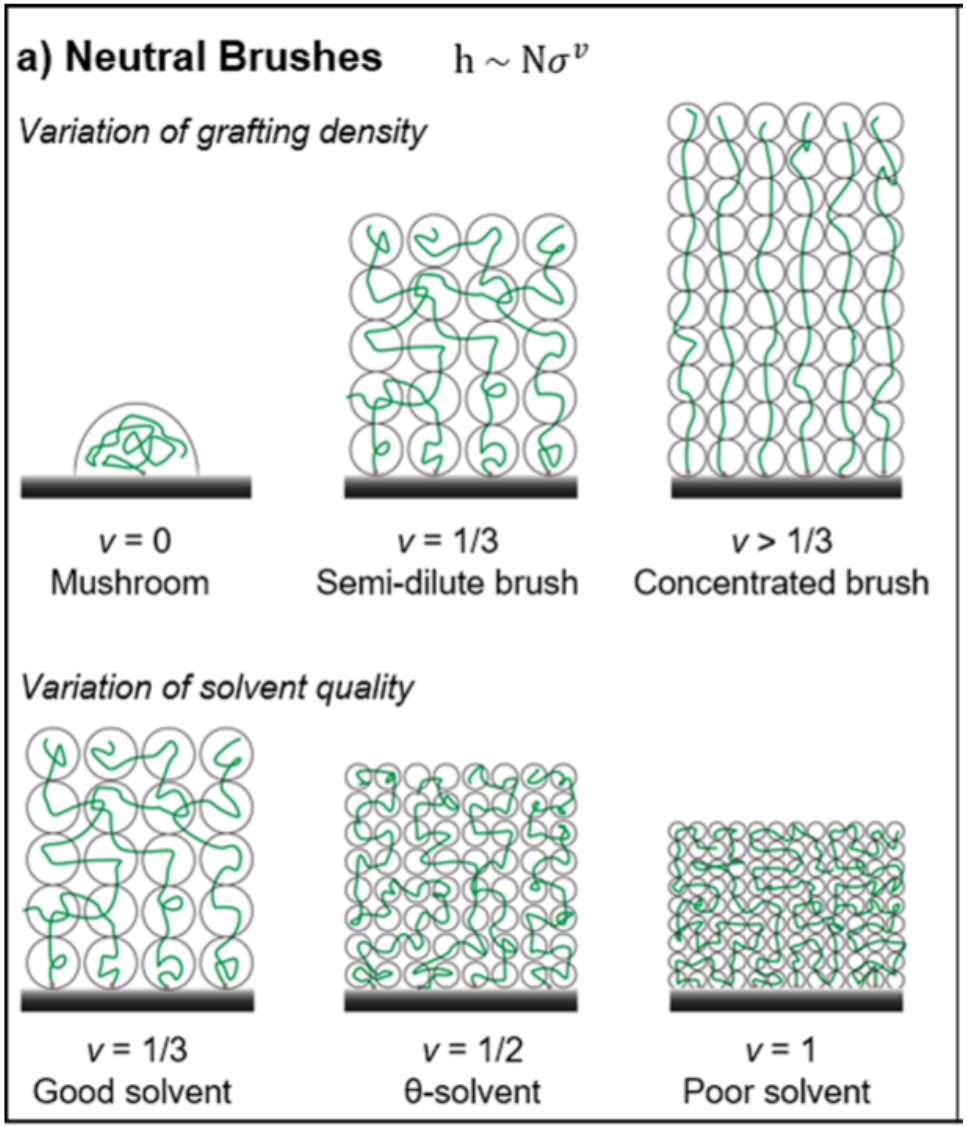
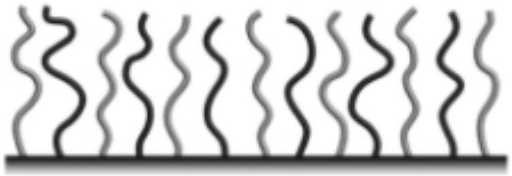
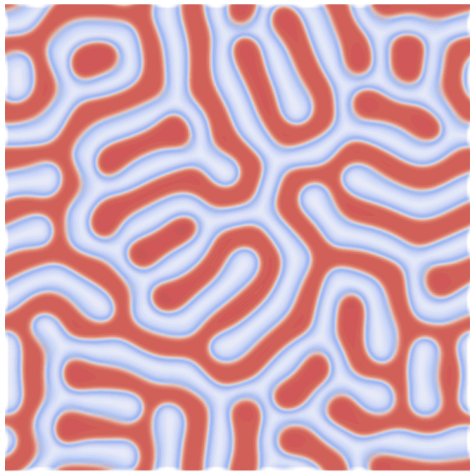


W.-L. Chen, R. Cordero, H. Tran, and C.K. Ober, Macromolecules **50**, 4089 (2017)

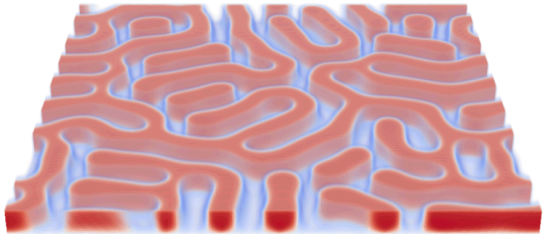
Mixed Polymer Brushes

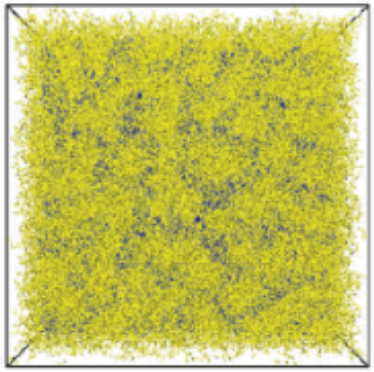
- multiple polymer species grafted to surface
- melt: highly stretched
- microphase separation
  - lateral
  - vertical



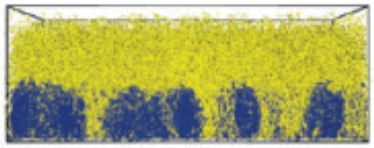


lateral phase separation





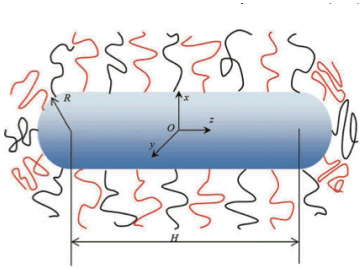
vertical phase separation

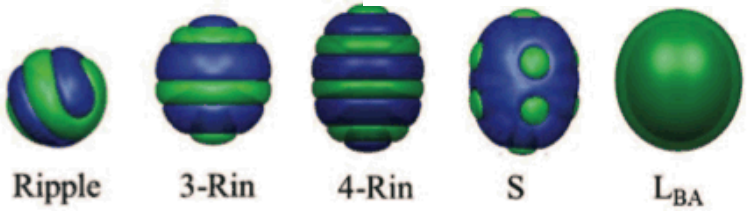


Wang, J. & Mueller, M. *J Phys Chem B* **113,** 11384–11402 (2009).

Applications for mixed brushes

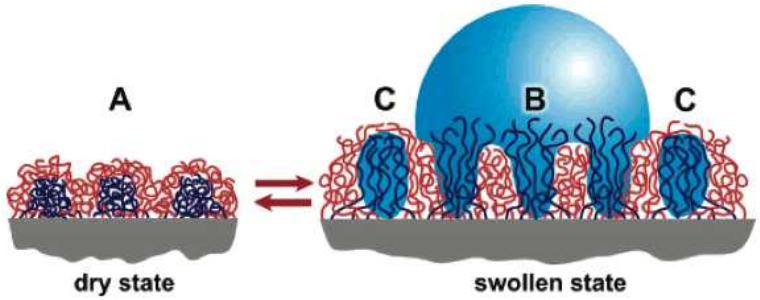
patchy nanoparticles





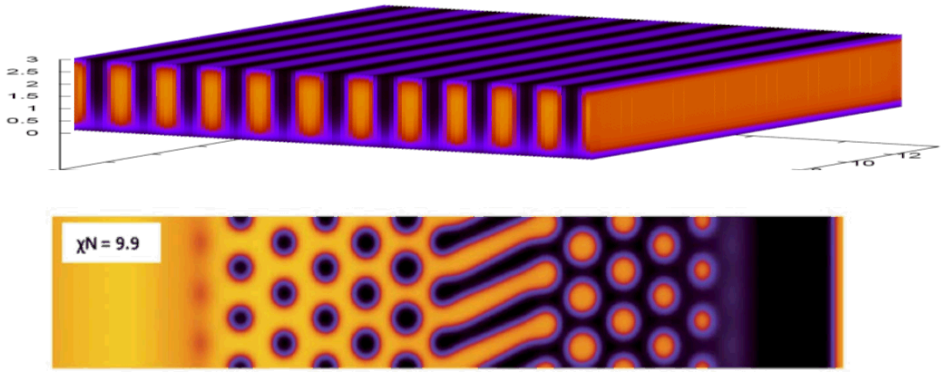
X. Ma, et al J Chem Phys **139**, 214902 (2013).

switchable surfaces



Motornov, M., Sheparovych, R., Tokarev, I., Roiter, Y. & Minko, S. *Langmuir* **23,** 13–19 (2007).

surface patterning



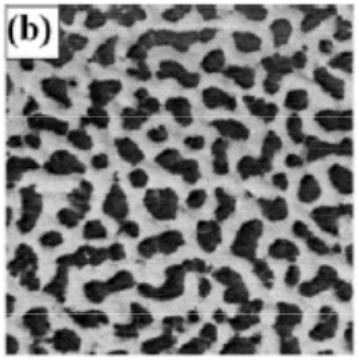
S-M. Hur, et al, *Soft Matter* **7**, 8776 (2011); *Soft Matter* **9**, 5341 (2013).

Binary brushes for nanolithography?

Sandia National Laboratories

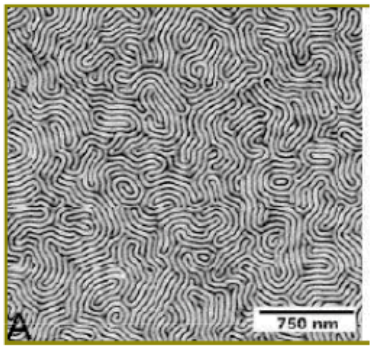
binary brushes phase separate similarly to diblock copolymer thin films

- "Ripple" phase of symmetric mixed brush (PS – PMMA) under non-selective solvent



Usov et al., *Macromolecules*, **2007**, *40*, 8774-8783

- Perpendicular lamella of PS-b-PMMA block copolymer thin film

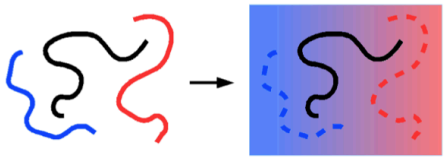


Daniel J.C. Herr, *Future Fab. Intl. Sec.5.* **2005**, Issue 18

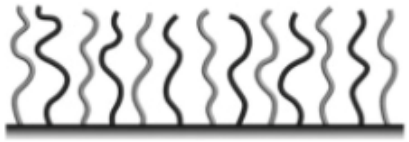
use brushes for patterning?
can we get long-range order?

Rest of the Talk

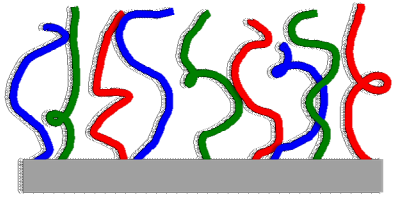
- polymer field theory



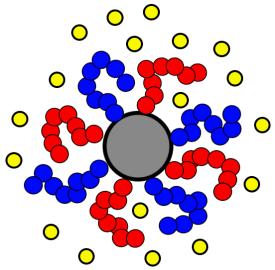
- binary brushes



- ternary brushes



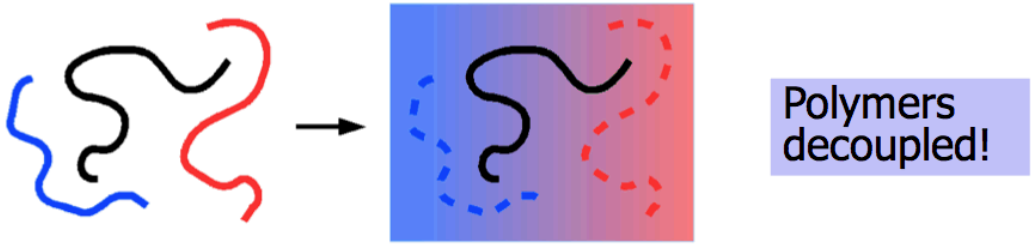
- binary brushes on nanoparticles



theme: effects of fluctuations

Self-Consistent Field Theory

- standard technique in polymer science
- replace interactions with many other polymers with interactions between 1 polymer and a field



interaction free energy between different polymers A and B:

$$U_{AB}/kT = \chi_{AB} \int d\mathbf{r} \rho_A(\mathbf{r}) \rho_B(\mathbf{r})$$

↓

Flory χ parameter

figure courtesy Glenn Fredrickson

Types of polymer field theory

1. a mean-field theory (SCFT) by making a *saddle point* approximation:

$$e^{-F} = Z = \int \mathcal{D}w e^{-H[w]} \approx e^{-H[w^*]} \qquad \left.\frac{\delta H[w]}{\delta w(r)}\right|_{w^*} = 0$$

- evaluate the partition function at the mean-field *w*: F ≈ H[w*]*
- accurate for high molecular weight melts

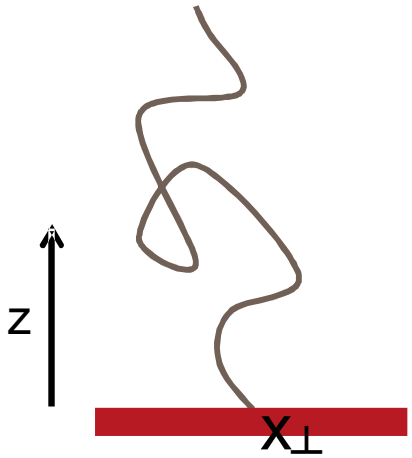
2. sample the entire partition function *Z*
   "field-theoretic simulations"

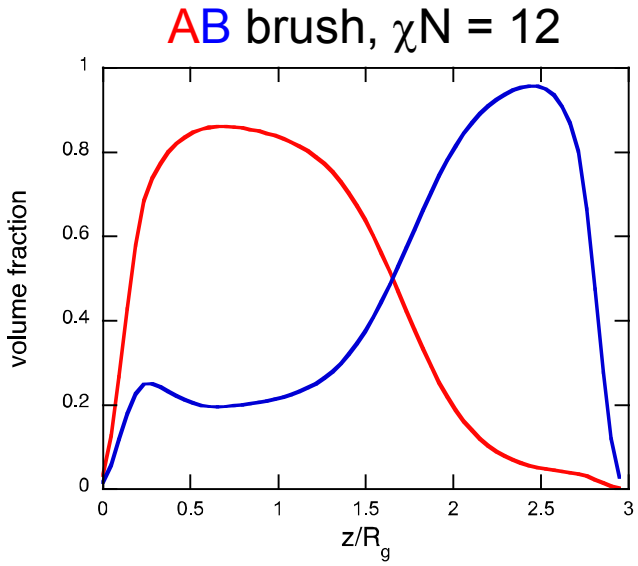
3. "dynamic mean field theory" (DMFT)—later in the talk

SCFT for Melt Polymer Brushes

- melt with high grafting density
- graft polymers of length N to surface
- large polymer/air surface tension so flat top surface
  - "walls" in z-direction (substrate + top surface)
  - assume brush height h = $3R_g$
- periodic boundaries in (x,y)
- polymers interaction strength: χN

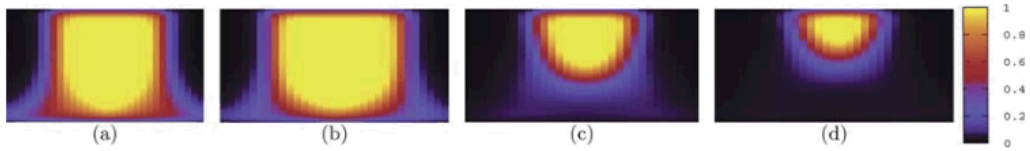
calculate minimum free energy from field theory





Calculation details

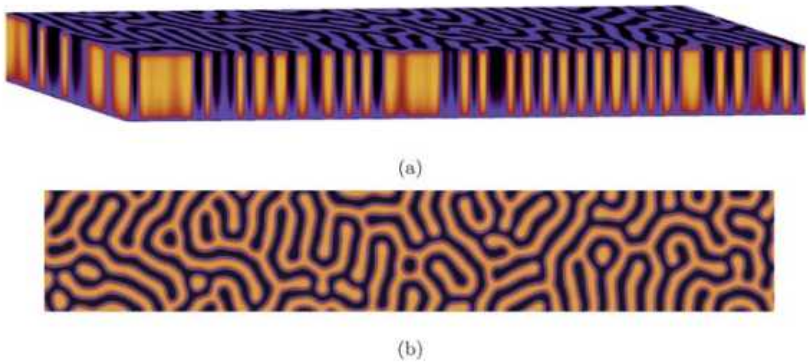
unit cell calculations



perform in small region
find box size in x, y dimensions with lowest free energy

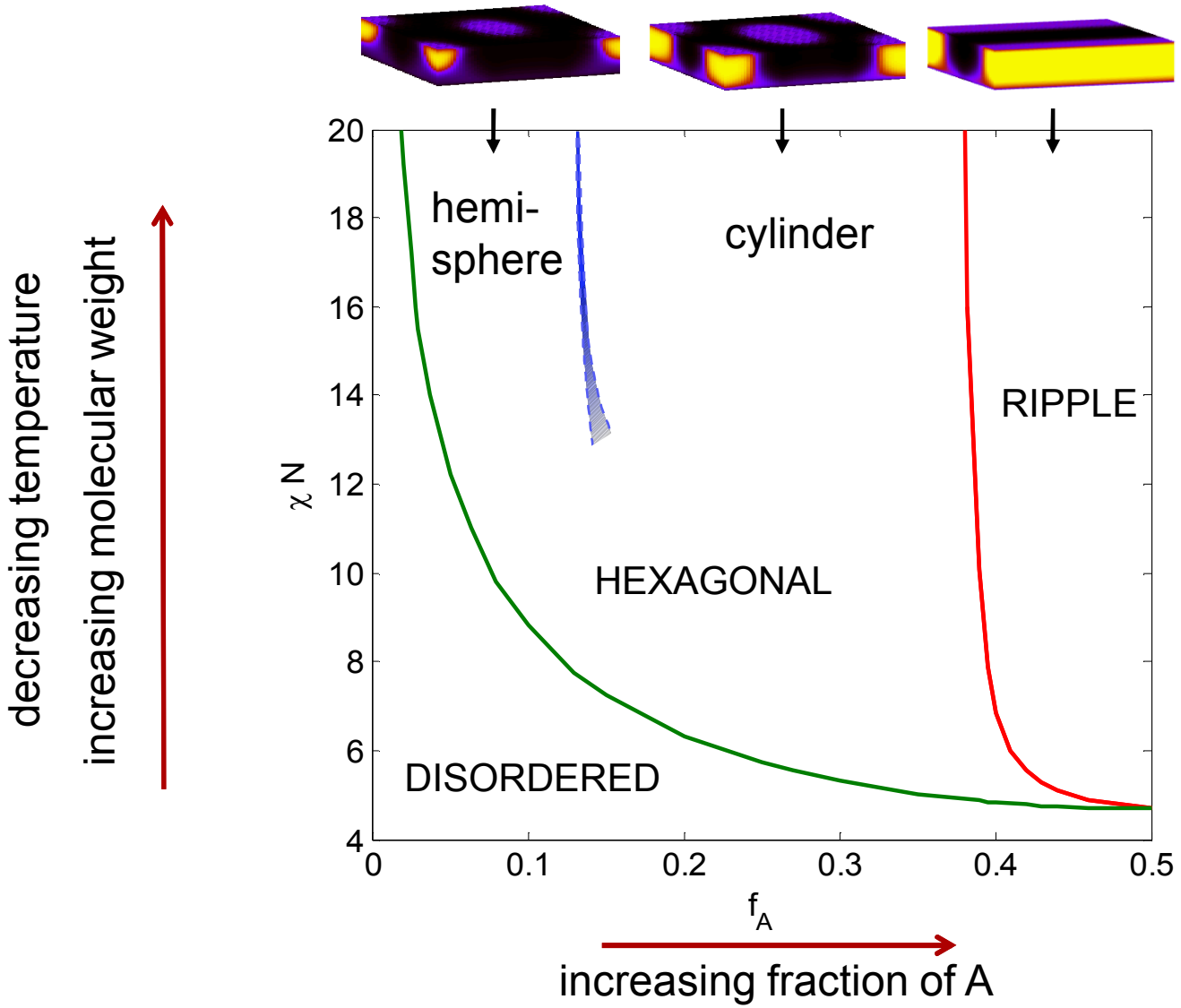
large cell simulations

start with random field configuration
iterate until free energy is “small”
equivalent to fast quench



S.-M. Hur, A.L. Frischknecht, D.L. Huber, and G.H. Fredrickson, Soft Matter **7**, 8776 (2011).

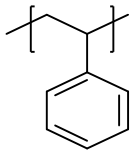
Phase Diagram of a Binary Melt Brush



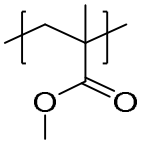
Experimental Verification

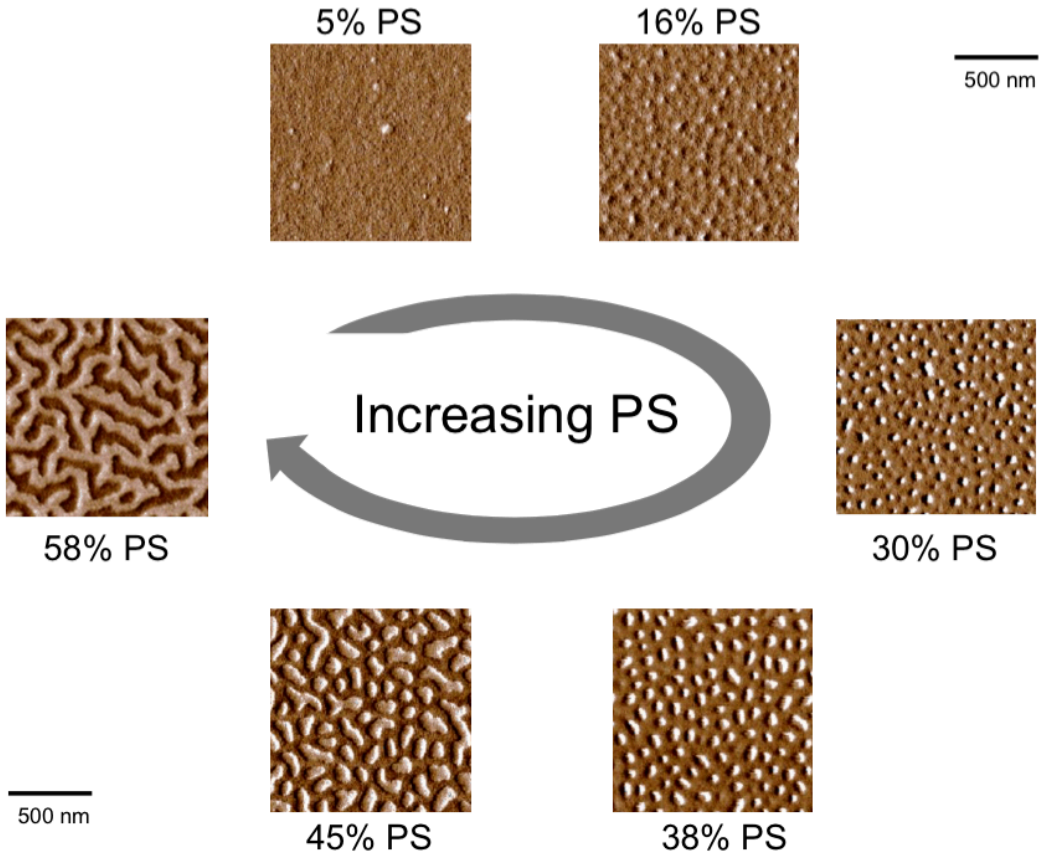
High Mw PS-PMMA mixed brushes
brush heights ≈ 30 nm

Polystyrene



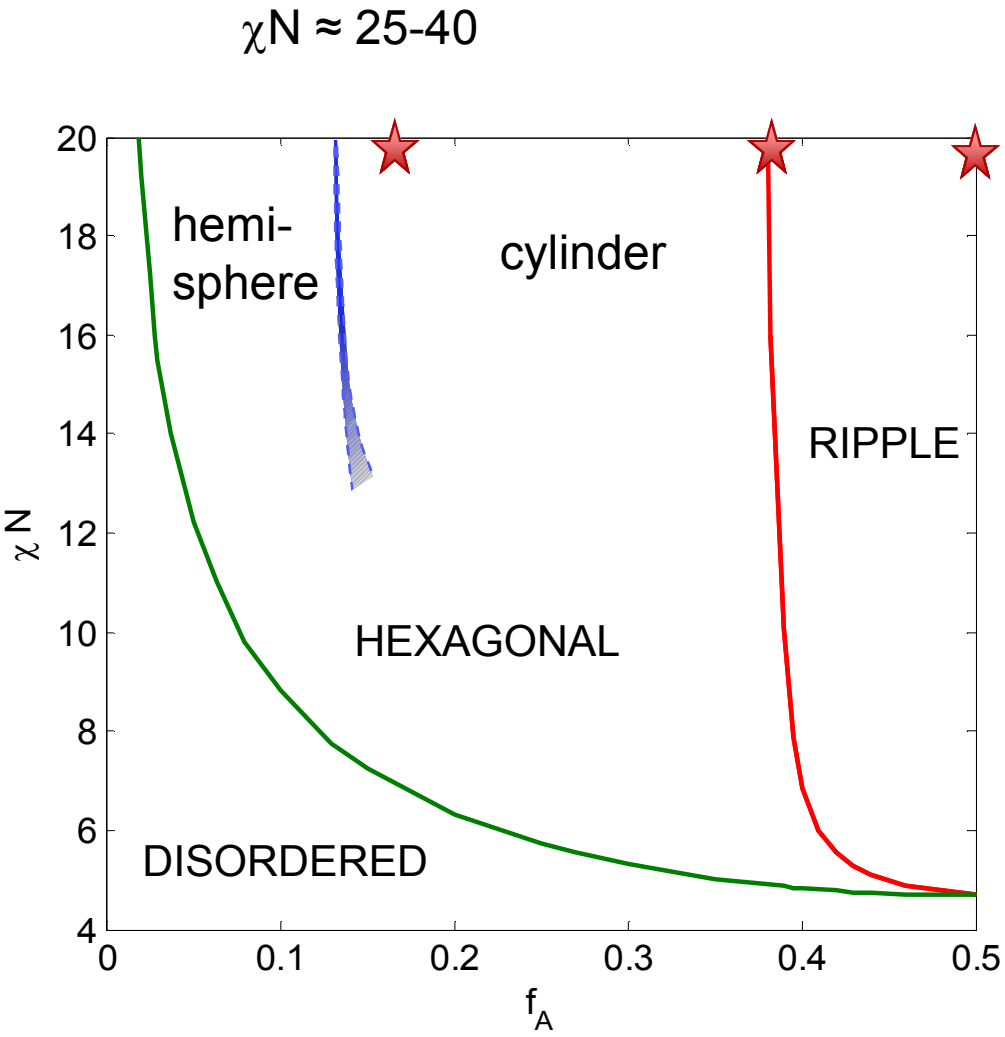
Poly(methyl methacrylate)



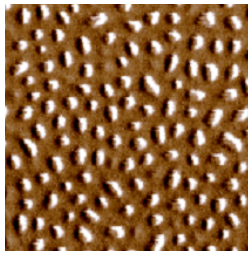


Price et al., *Macromolecules* **45**, 510 (2012)

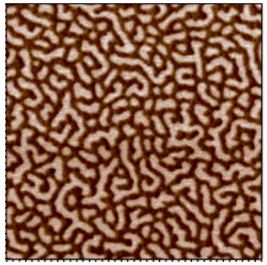
Experimental Phases Similar to Theory



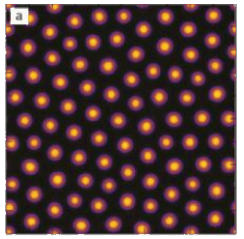
16% PS



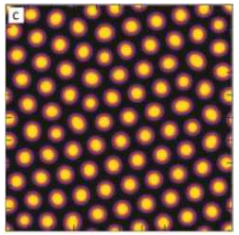
38% PS



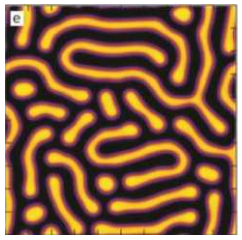
51% PS



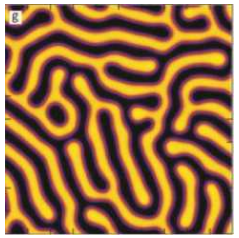
10%



30%



40%



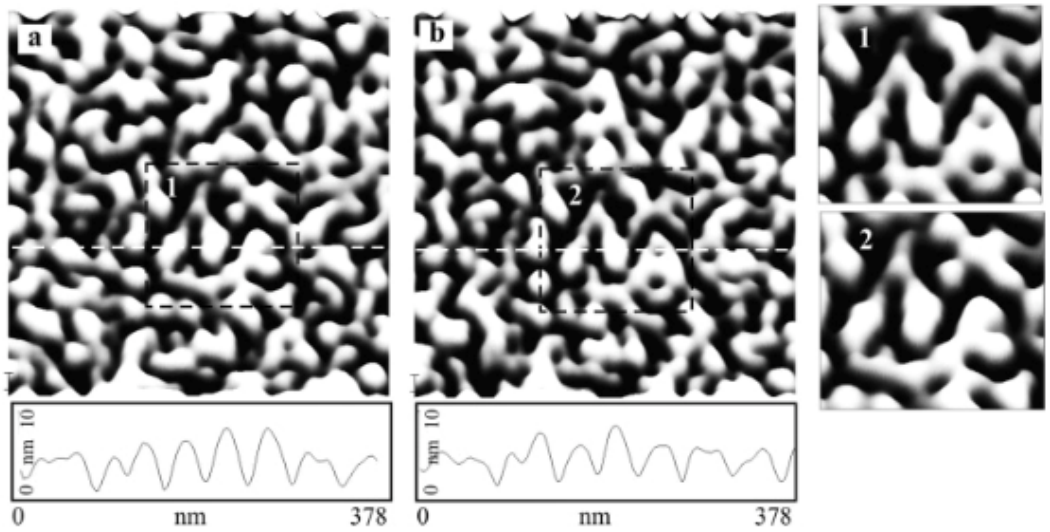
50%

Why no long range order?

theory assumes *uniform* distribution of grafting sites

experimentally: *random* is not the same as *uniform*

fluctuations in grafting density lead to disorder in lateral structure



memory effect: domains reform in same location after solvent cycle

S. Santer, A. Kopyshev, J. Donges, J. Ruehe, X. Jiang, B. Zhao, and M. Mueller, Langmuir **23**, 279 (2007).

Grafting density fluctuations

incorporate spatial variations in grafting density in theory

SCFT

uniform grafting density

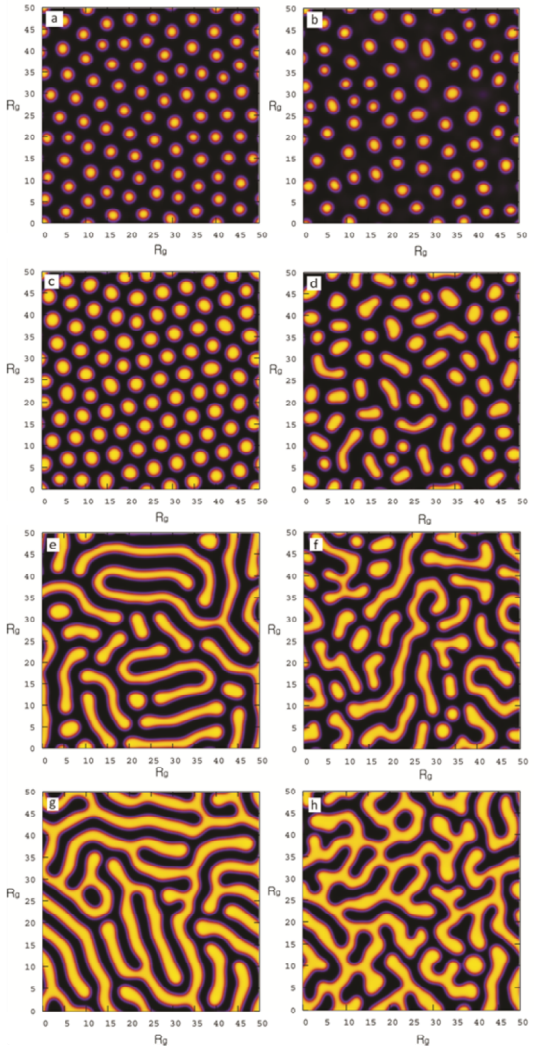
$$g_A(\mathbf{x}_\perp) = f_A$$

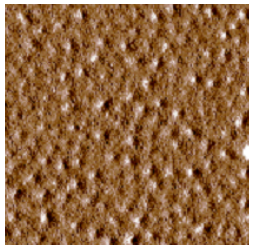
Gaussian random distribution of grafting sites

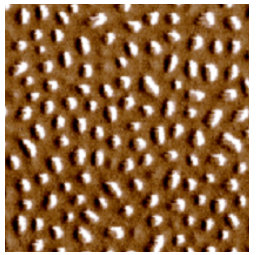
$$\langle (g_A(\mathbf{x}_\perp) - f_A)(g_A(\mathbf{x'}_\perp) - f_A) \rangle = \Lambda^2 \exp(-|\mathbf{x}_\perp - \mathbf{x'}_\perp|^2/2\sigma^2)$$

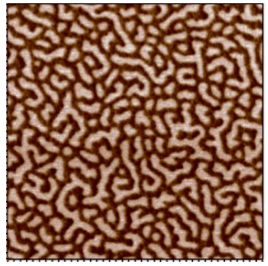
$\sigma = 0.5R_g$, $\Lambda^2 = 0.02$

uniform correlated experiment









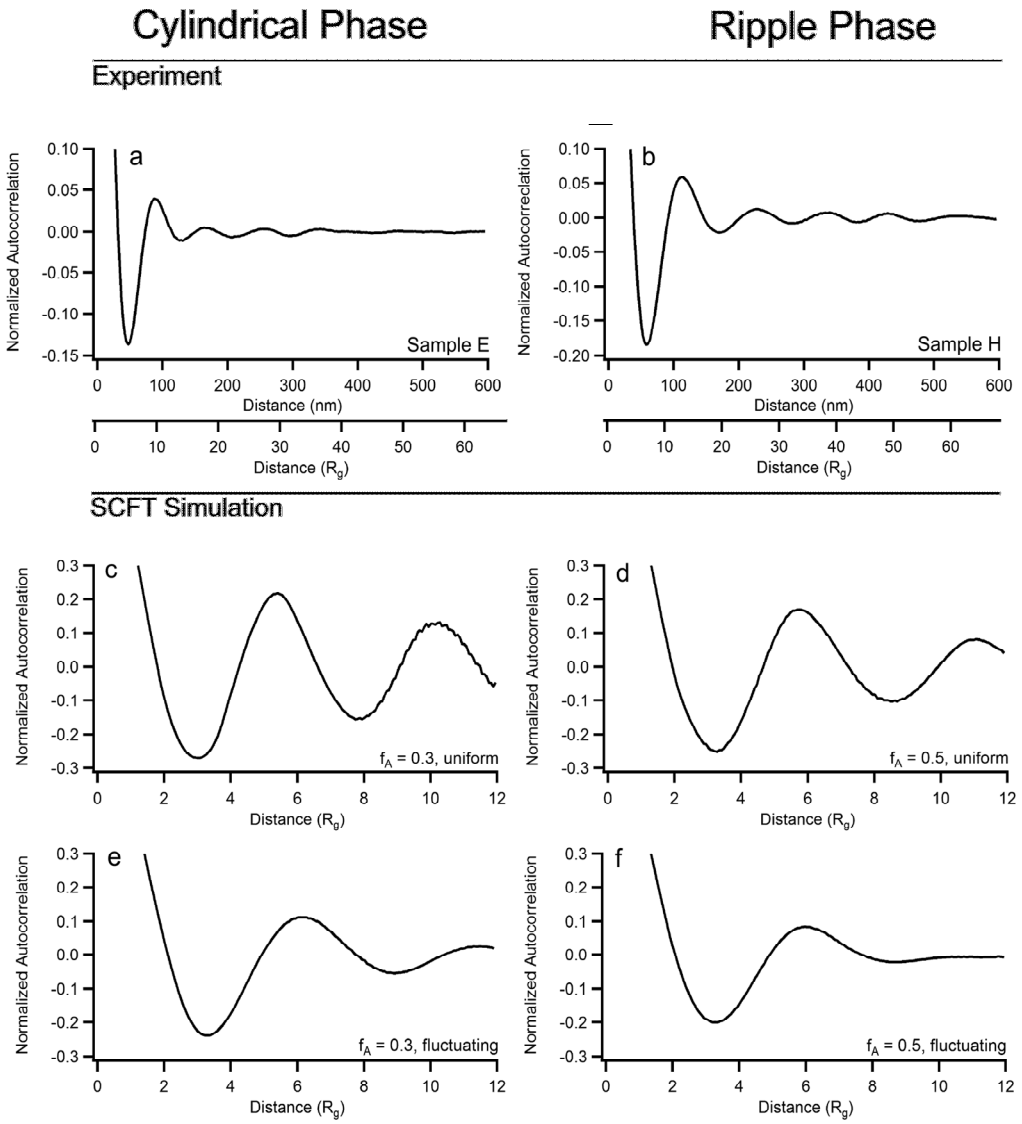
Price et al., *Macromolecules* **45**, 510 (2012); Hur et al., *Soft Matter* **9**, 5341 (2013)

Similar amounts of order

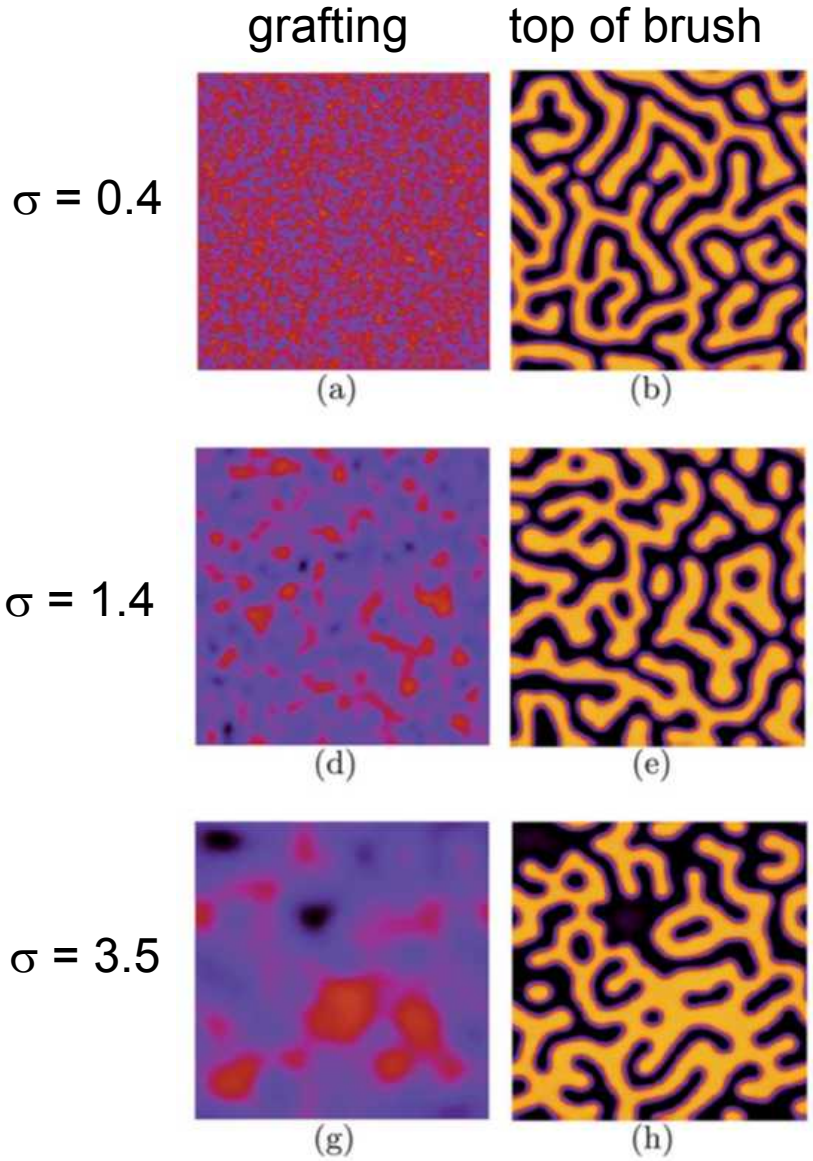
Sandia National Laboratories

experiment

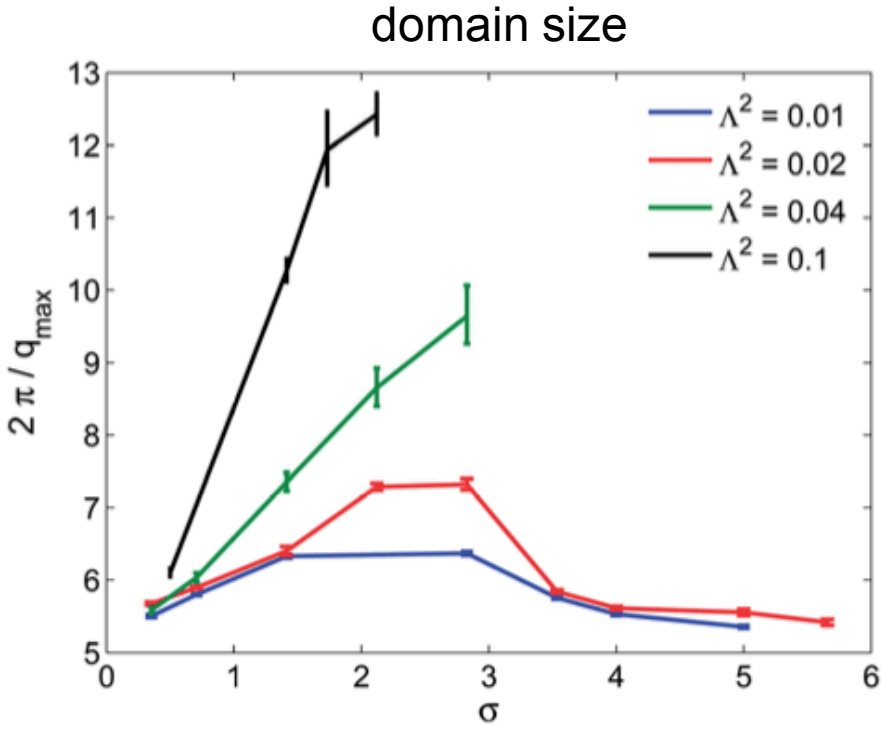
simulations



Correlations in grafting density



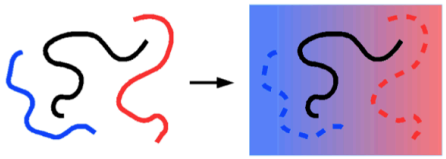
$$\langle (g_A(\mathbf{x}_\perp) - f_A)(g_A(\mathbf{x'}_\perp) - f_A) \rangle = \Lambda^2 \exp(-|\mathbf{x}_\perp - \mathbf{x'}_\perp|^2 / 2\sigma^2)$$



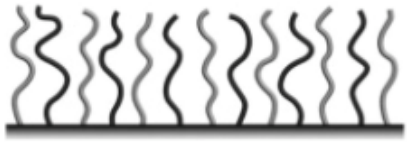
Hur et al., *Soft Matter* **9**, 5341 (2013)

Rest of the Talk

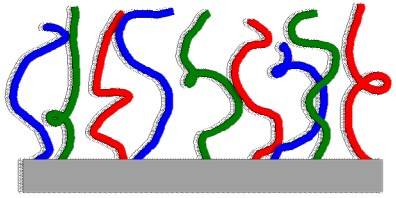
- polymer field theory



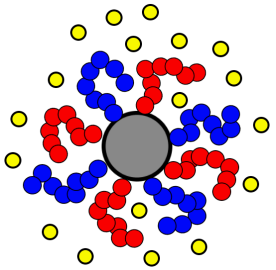
- binary brushes



- ternary brushes



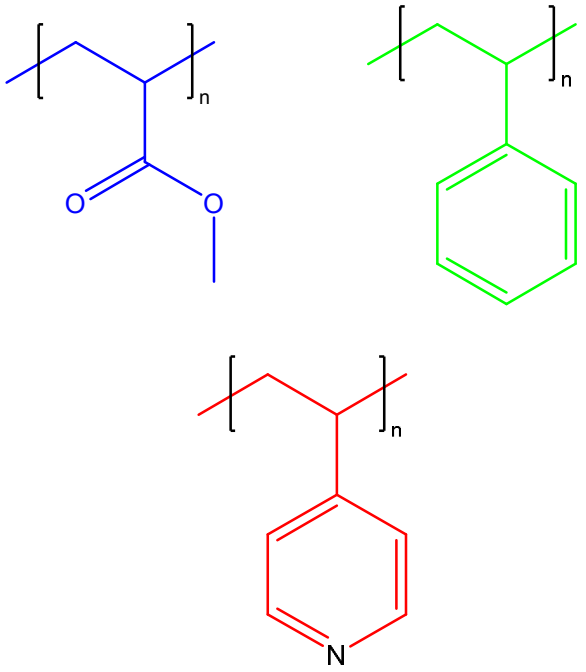
- binary brushes on nanoparticles

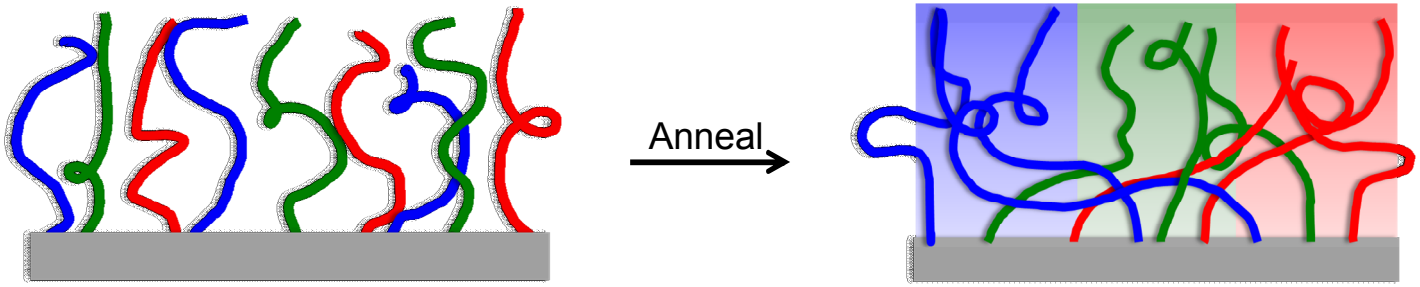


theme: effects of fluctuations

Ternary Polymer Brushes

- PMMA, PS, and P4VP
- Strongly segregating system
  - $\chi N_{PS\text{-}PMMA} \approx 18$
  - $\chi N_{PMMA\text{-}P4VP} \approx 65$
  - $\chi N_{PS\text{-}P4VP} \approx 320$
- AFM was used to analyze phase behavior





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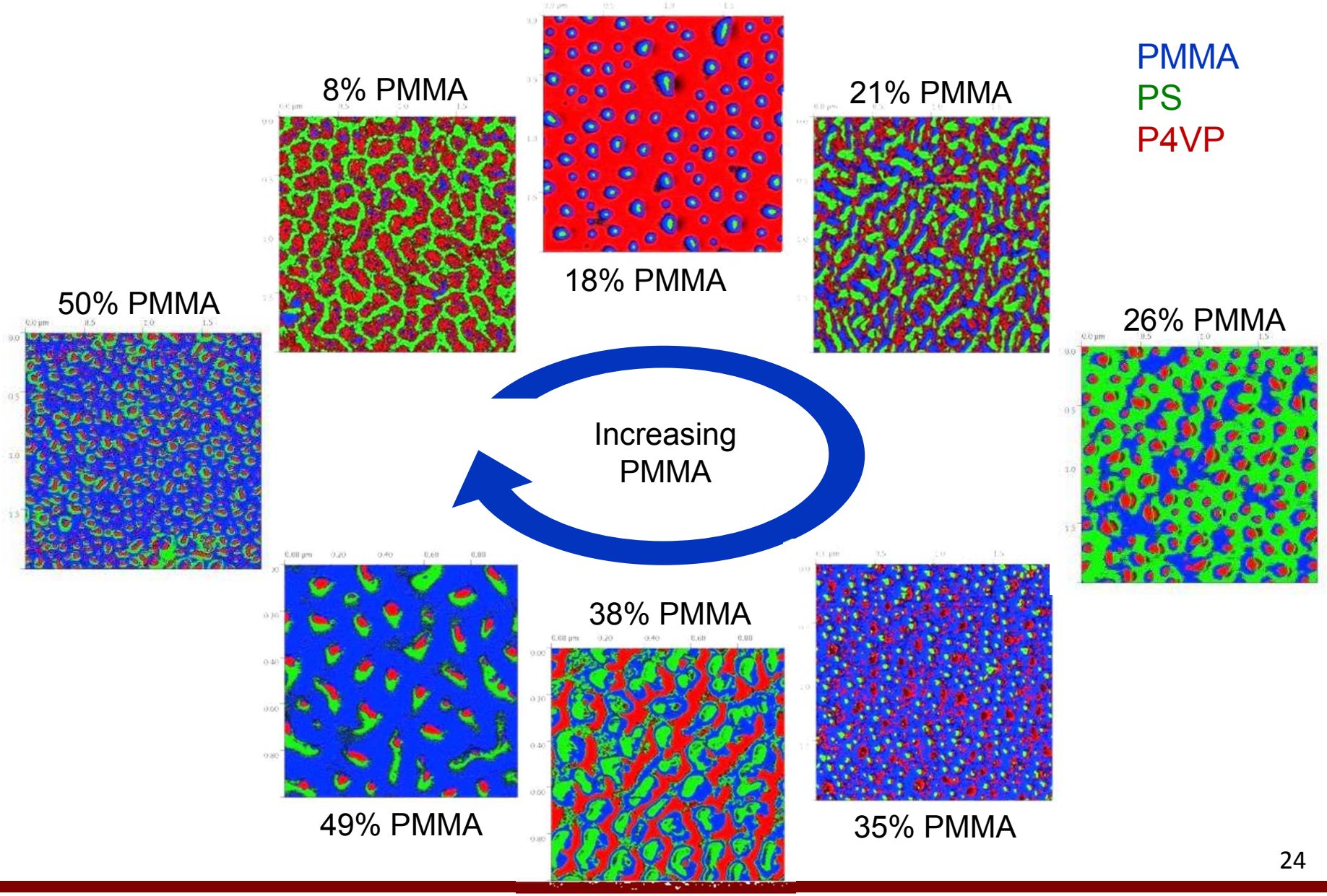
Experimental Phase Behavior



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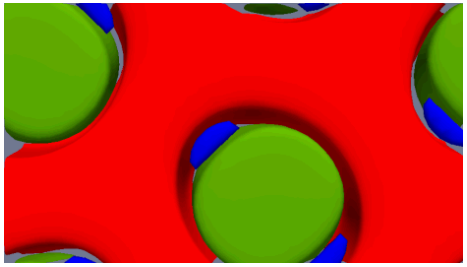
Unit Cell SCFT Calculations

set $\chi N_{AB} = 10$, $\chi N_{AC} = 12$, $\chi N_{BC} = 16$

10% PMMA



Decorated Cylinder

PMMA
PS
P4VP

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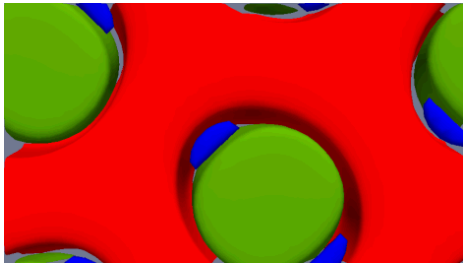
Unit Cell SCFT Calculations

10% PMMA



Decorated Cylinder

10% PMMA

Decorated Ripple

PMMA
PS
P4VP

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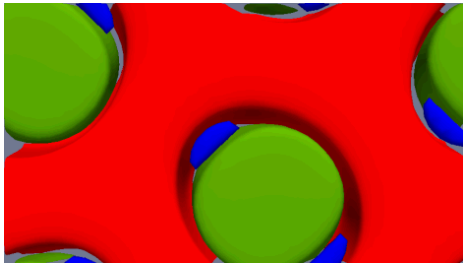
Unit Cell SCFT Calculations

10% PMMA

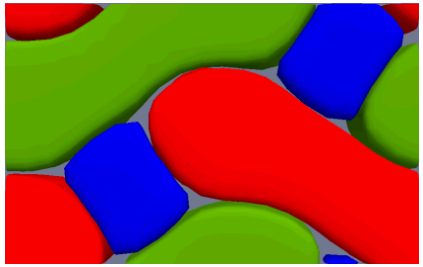


Decorated Cylinder

10% PMMA

Decorated Ripple

20% PMMA



Basket Weave

PMMA
PS
P4VP

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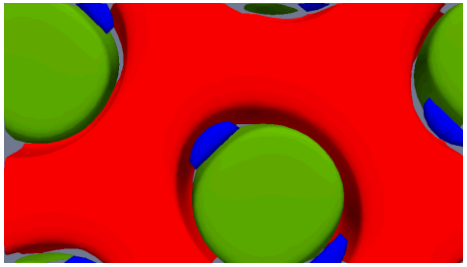
Unit Cell SCFT Calculations

10% PMMA

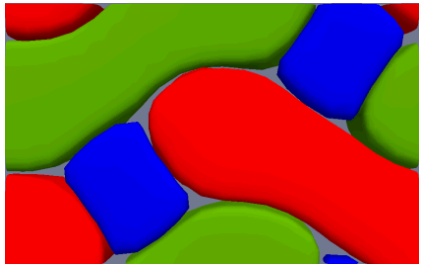


Decorated Cylinder

10% PMMA

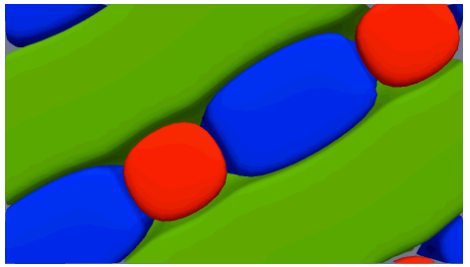
Decorated Ripple

20% PMMA



Basket Weave

30% PMMA



Segmented Ripple

PMMA
PS
P4VP

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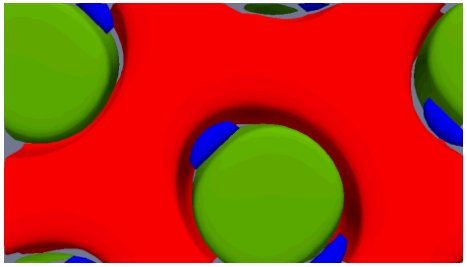
Unit Cell SCFT Calculations

10% PMMA

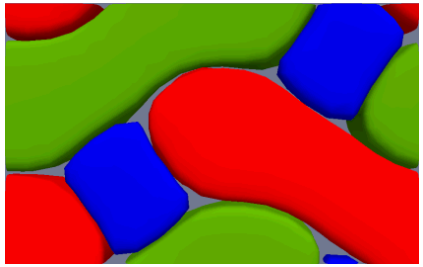


Decorated Cylinder

10% PMMA

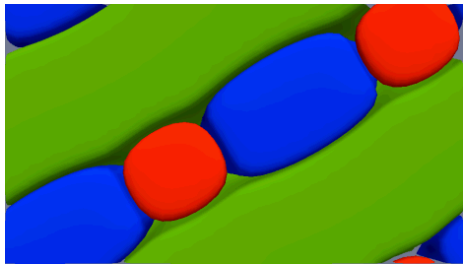
Decorated Ripple

20% PMMA

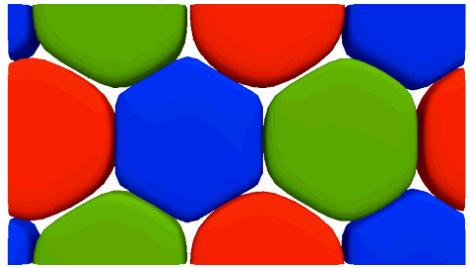


Basket Weave

30% PMMA



Segmented Ripple



Checkerboard

33% PMMA

PMMA
PS
P4VP

Increasing PMMA

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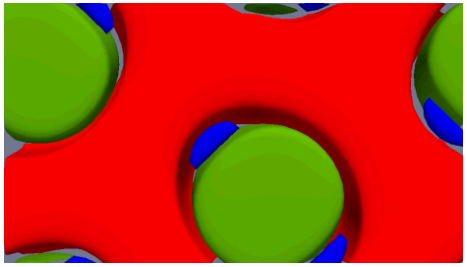
Unit Cell SCFT Calculations

10% PMMA

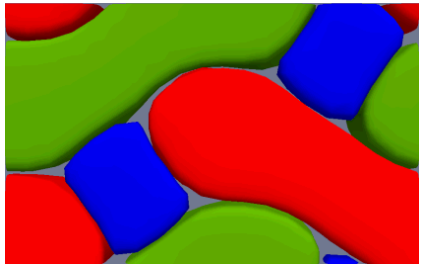


Decorated Cylinder

10% PMMA

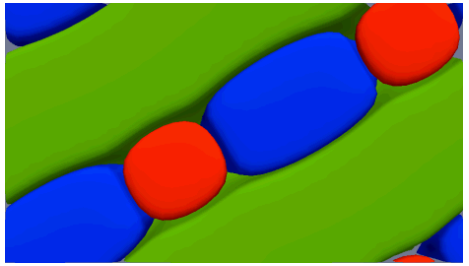
Decorated Ripple

20% PMMA



Basket Weave

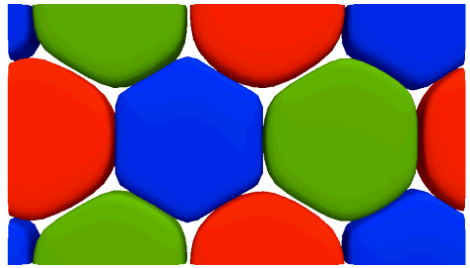
30% PMMA



Segmented Ripple

PMMA
PS
P4VP

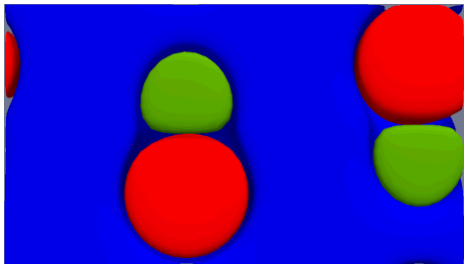
Increasing PMMA



33% PMMA

Checkerboard

70% PMMA



Lobed Cylinder

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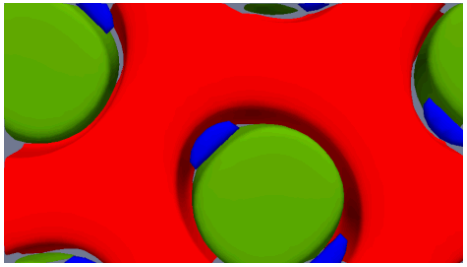
Unit Cell SCFT Calculations

Sandia National Laboratories

10% PMMA

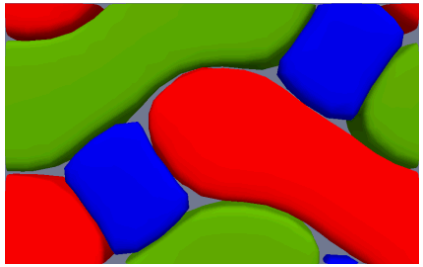
Decorated Ripple

10% PMMA



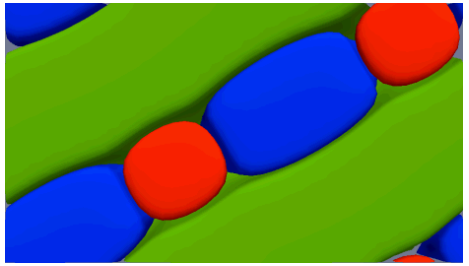
Decorated Cylinder

20% PMMA



Basket Weave

30% PMMA

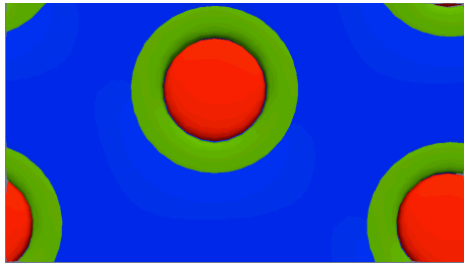


Segmented Ripple

PMMA
PS
P4VP

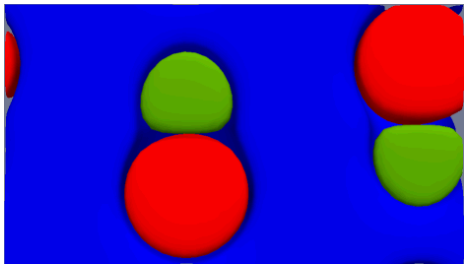
Increasing PMMA

Ringed Cylinder

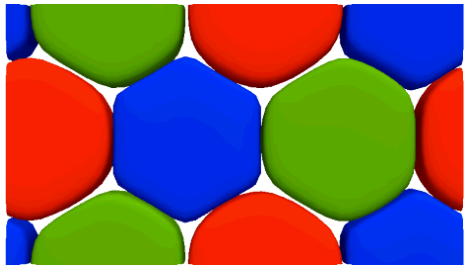


80% PMMA

70% PMMA



Lobed Cylinder



33% PMMA

Checkerboard

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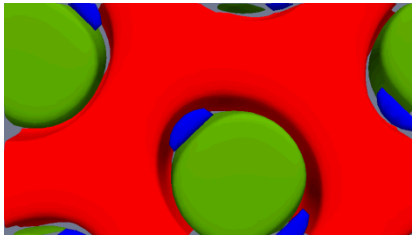
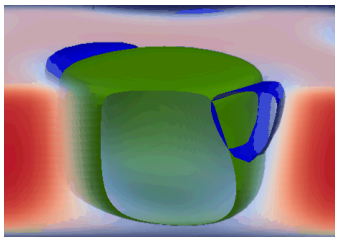
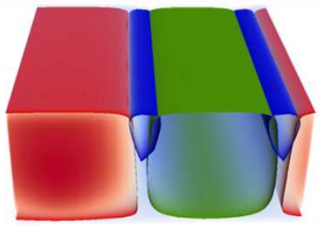
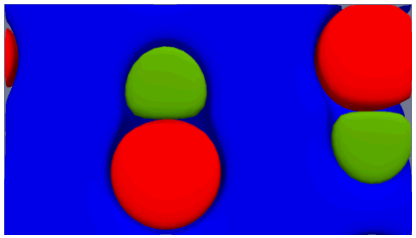
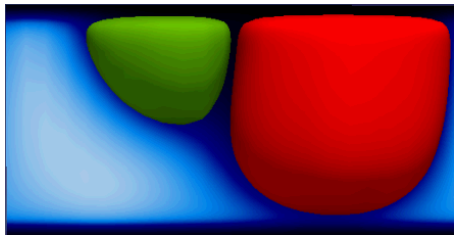
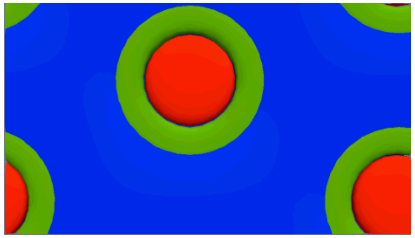
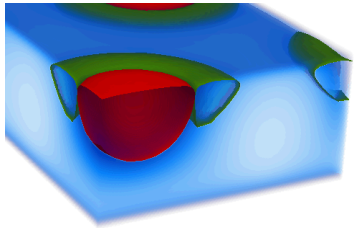
Below the Surface

	PMMA	PS	P4VP	
	0.1	0.3	0.6	
	0.1	0.4	0.5	
	0.7	0.1	0.2	
	0.8	0.1	0.1	

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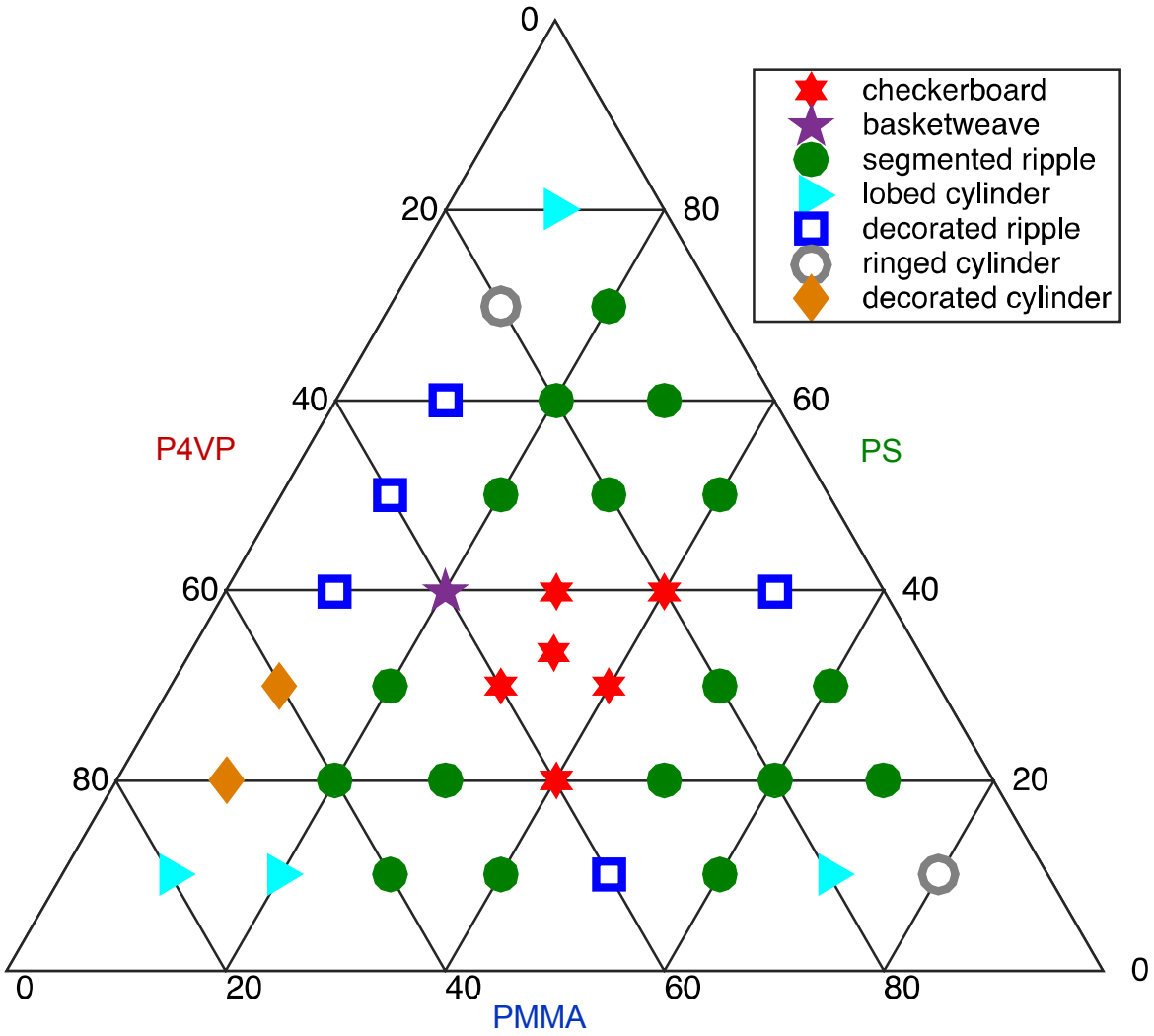
Phase Diagram



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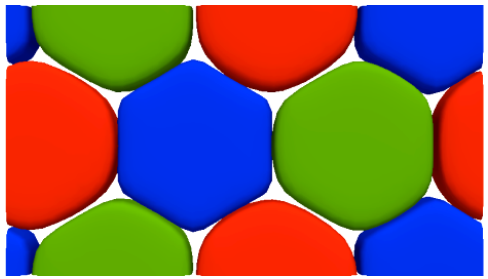
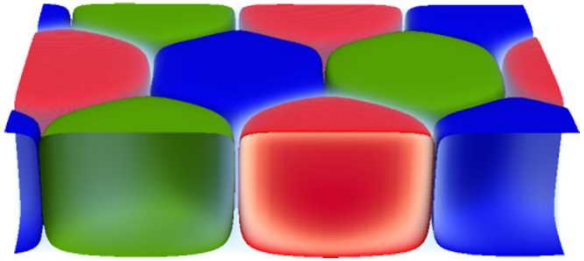
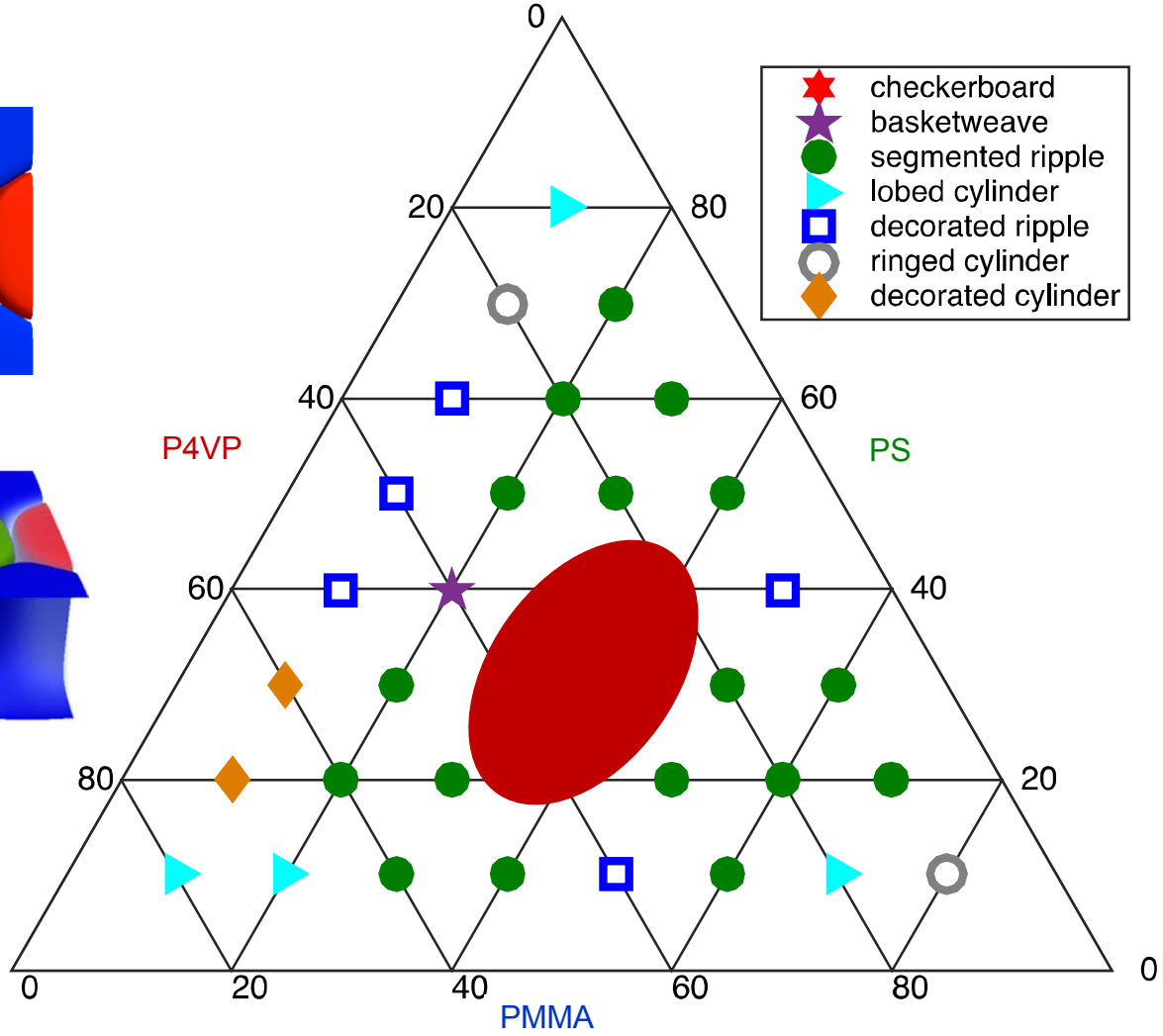
Phase Diagram







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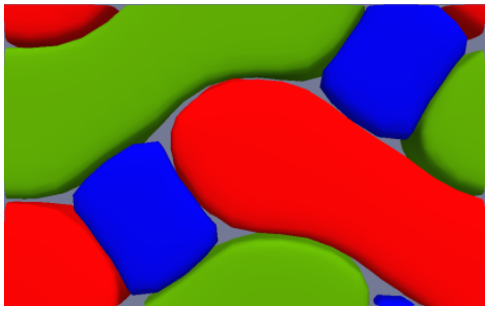
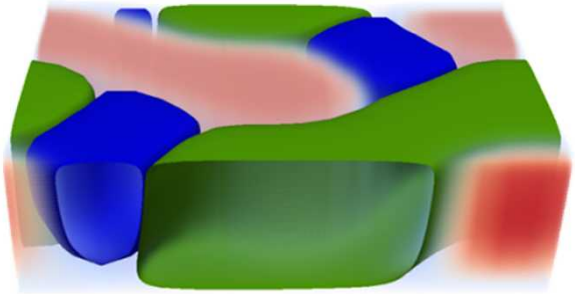
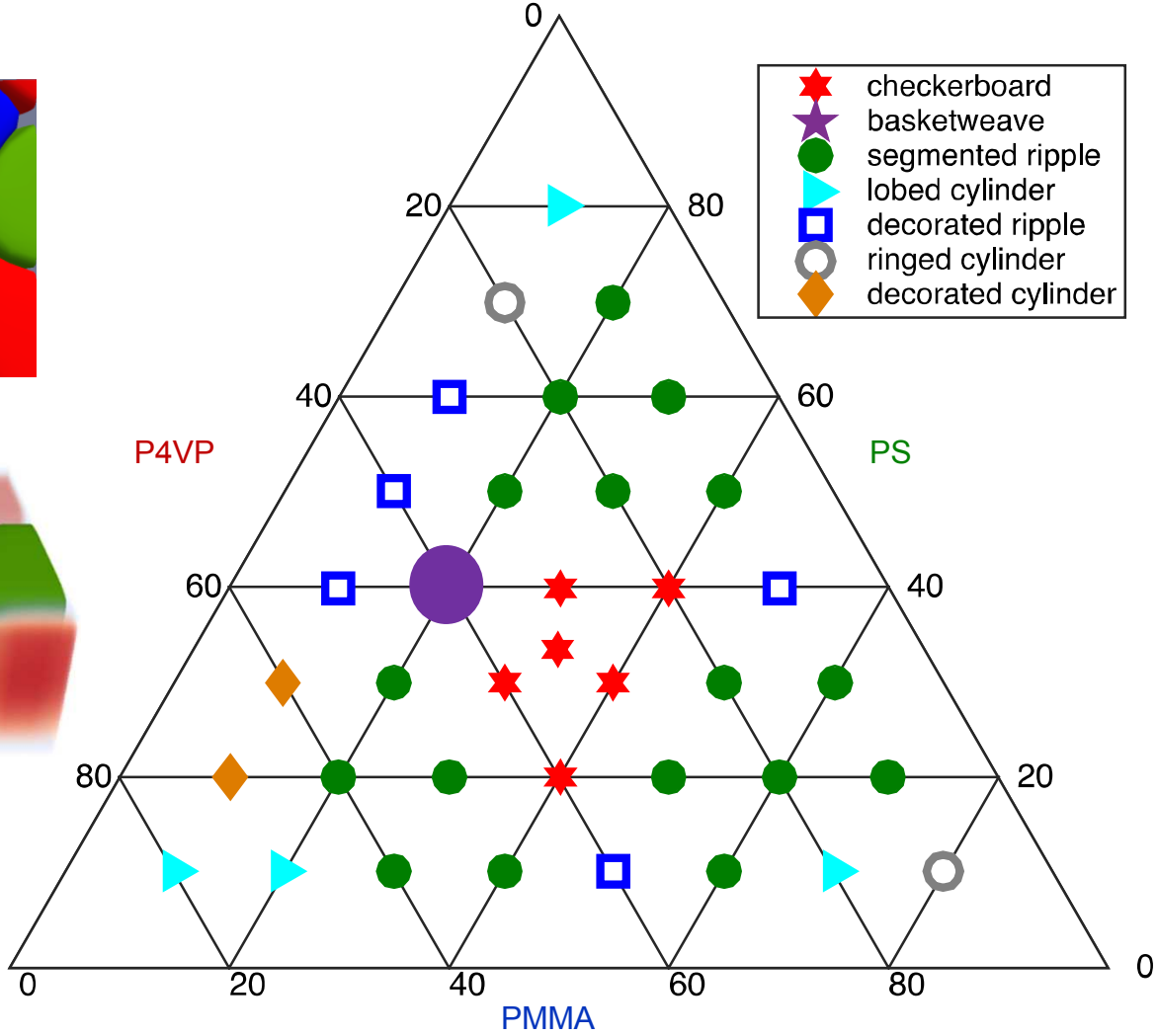
Phase Diagram







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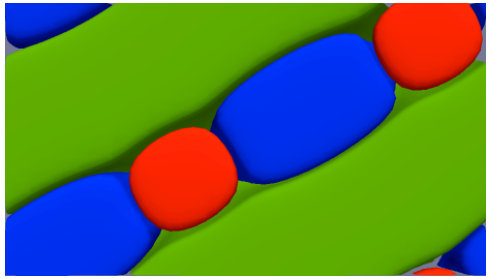
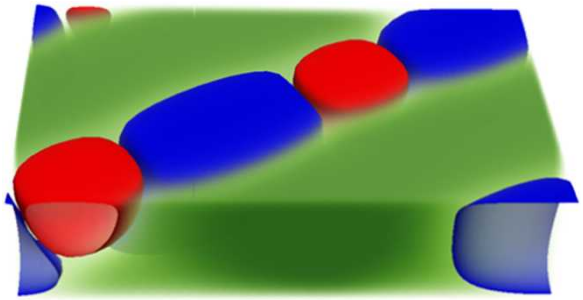
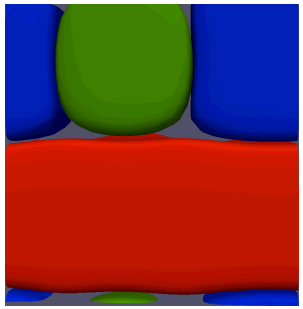
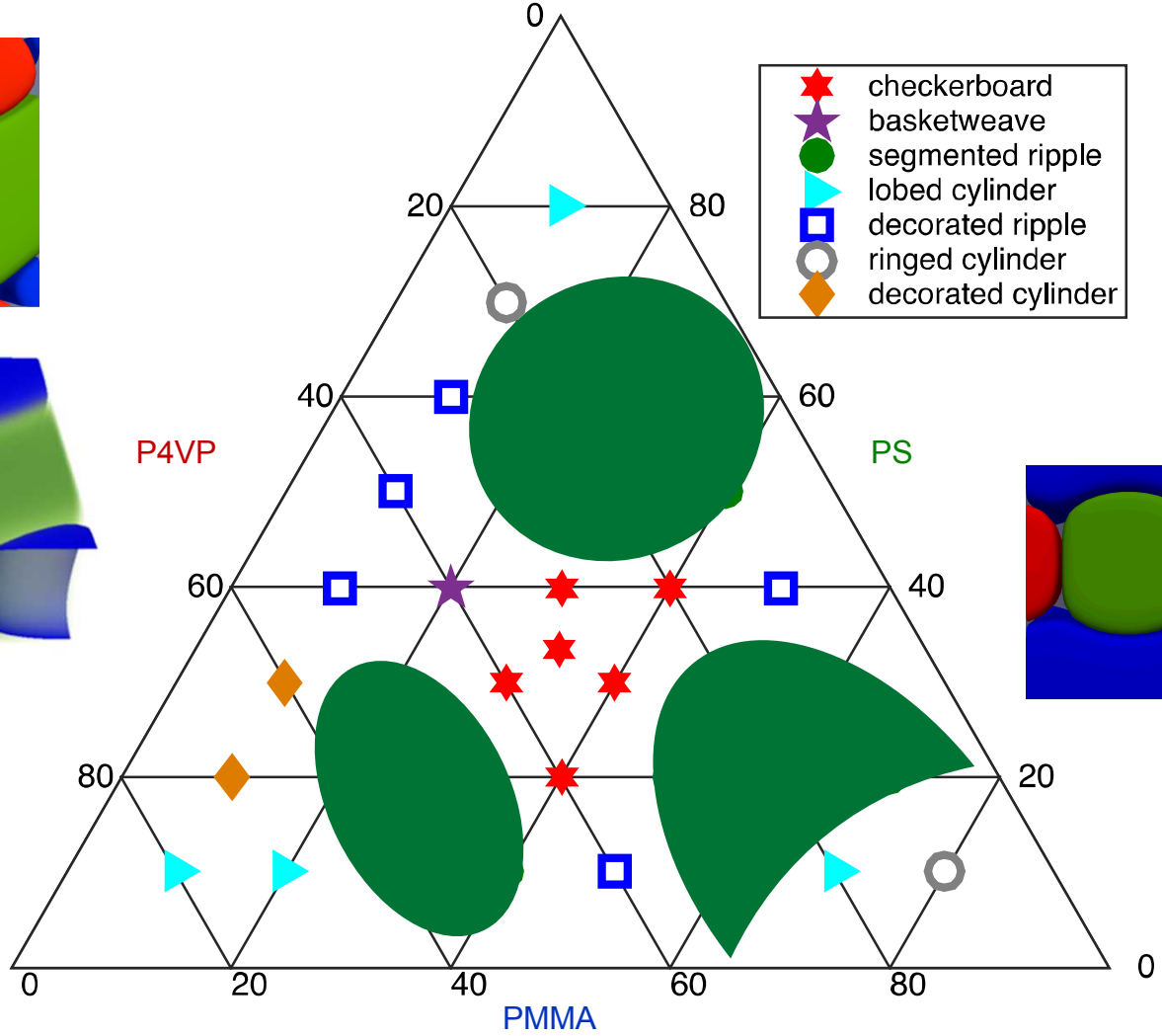
Phase Diagram









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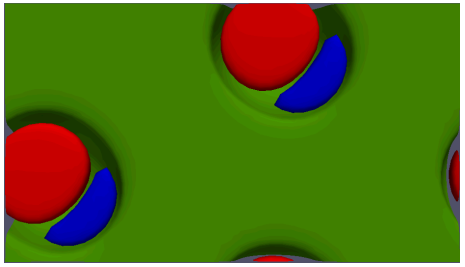
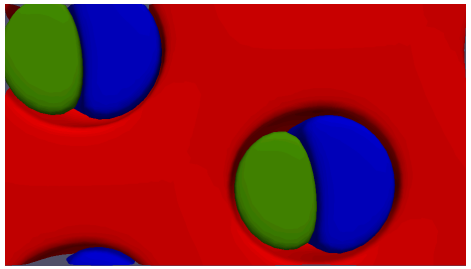
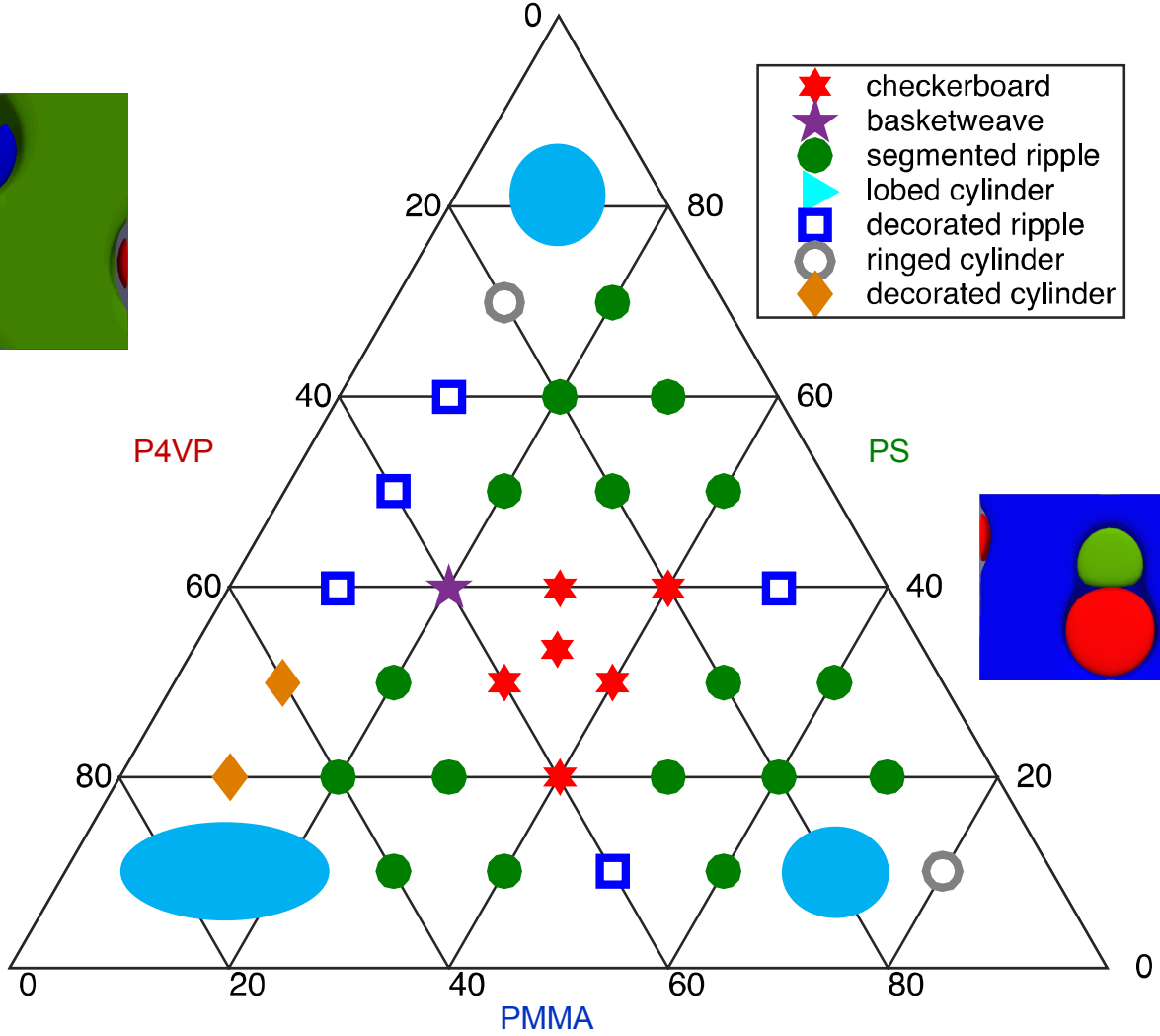
Phase Diagram







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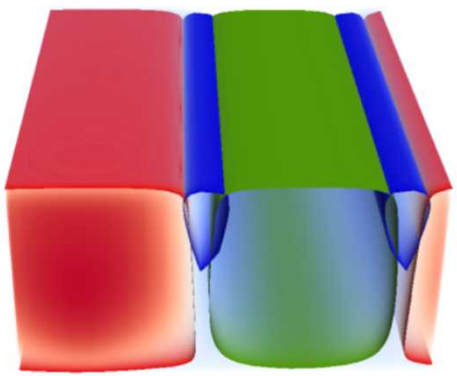
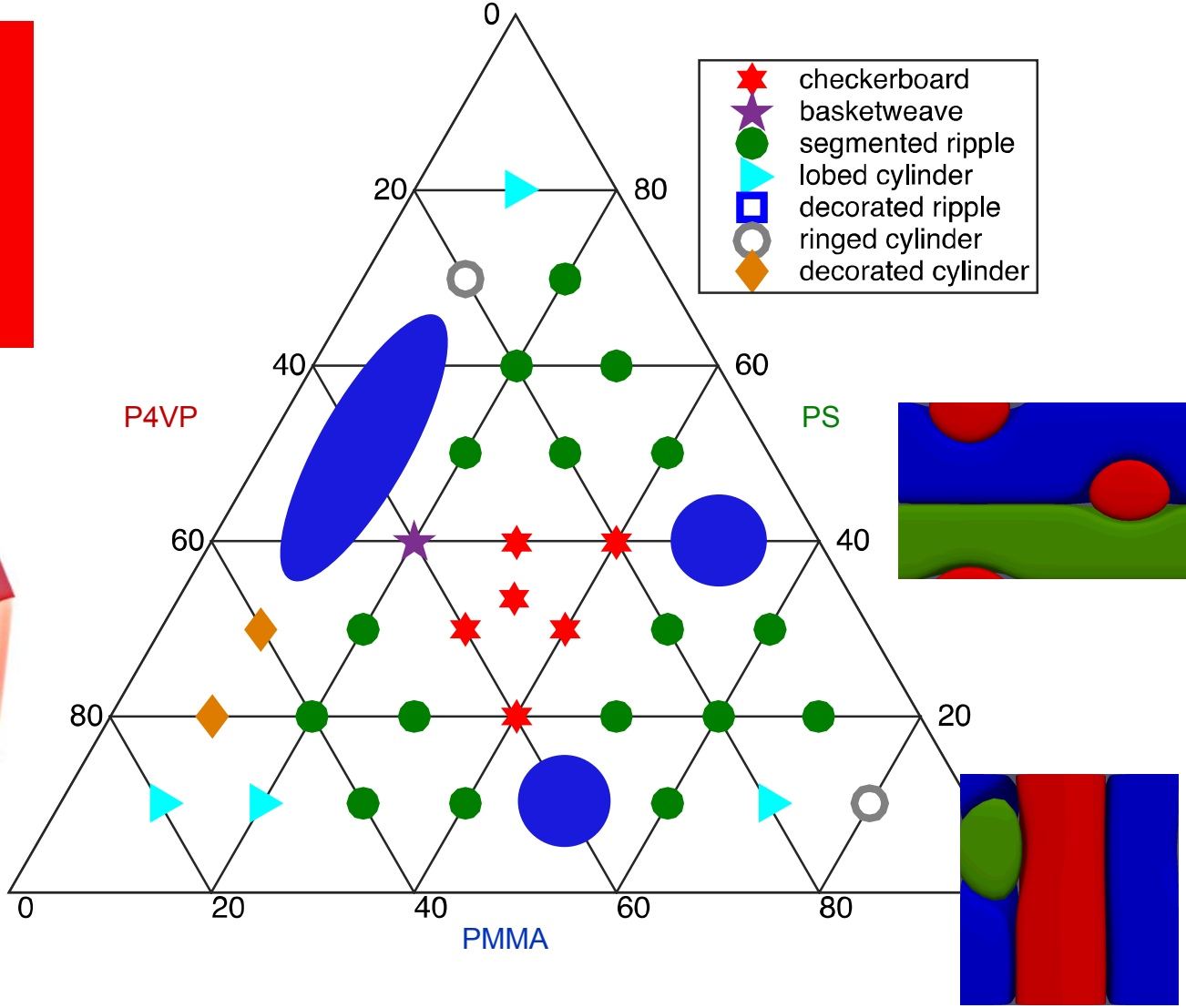
Phase Diagram





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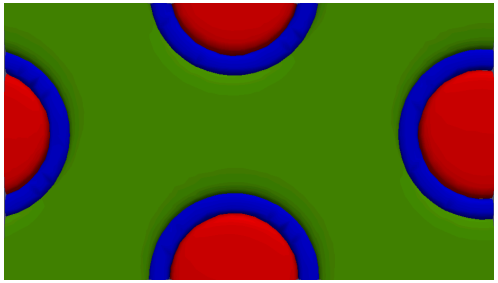
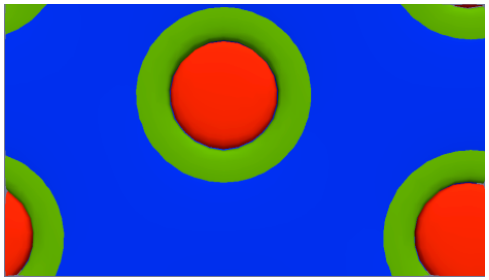
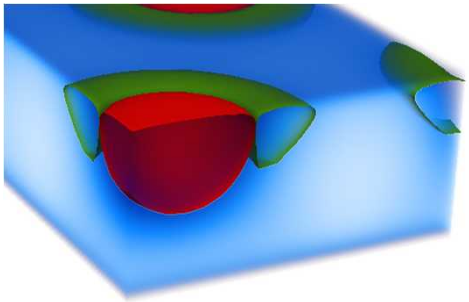
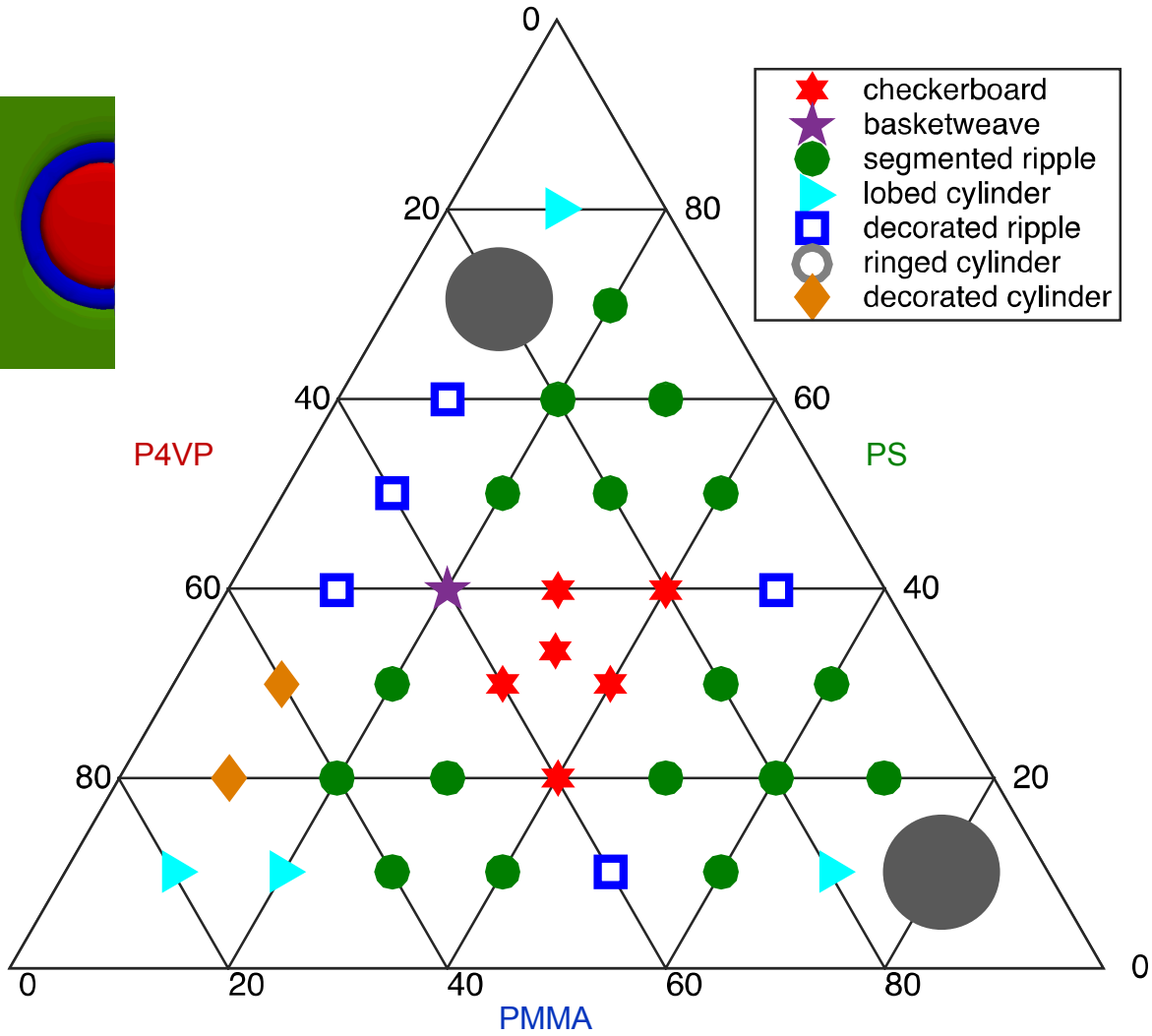
Phase Diagram









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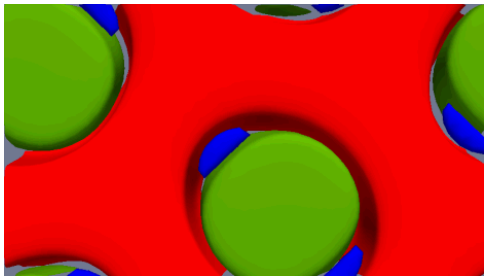
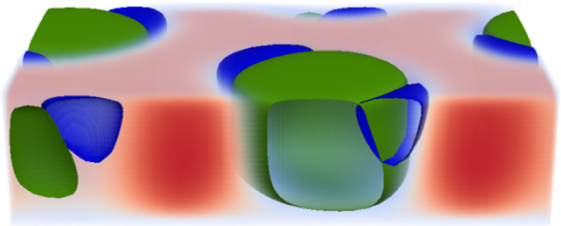
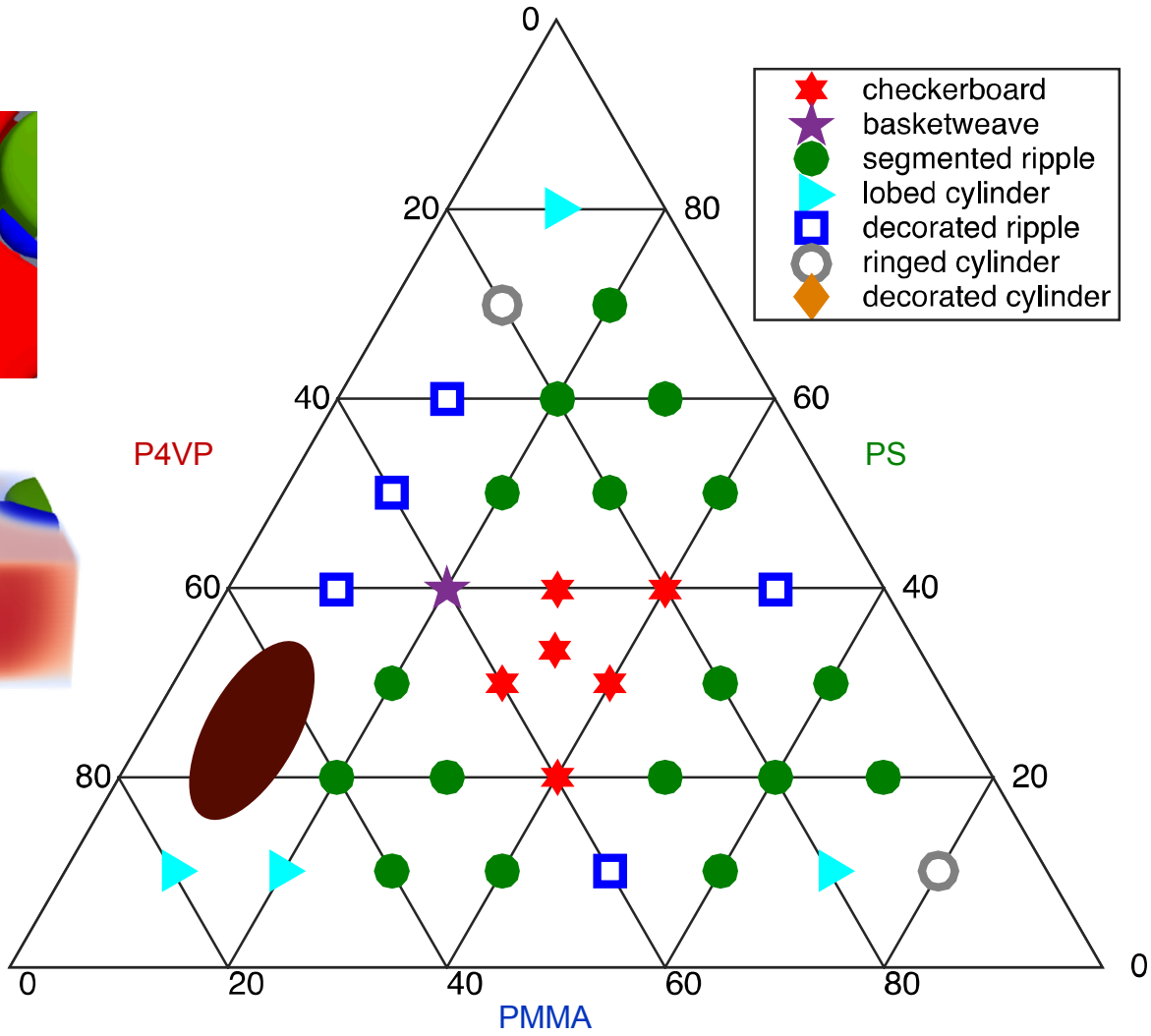
Phase Diagram







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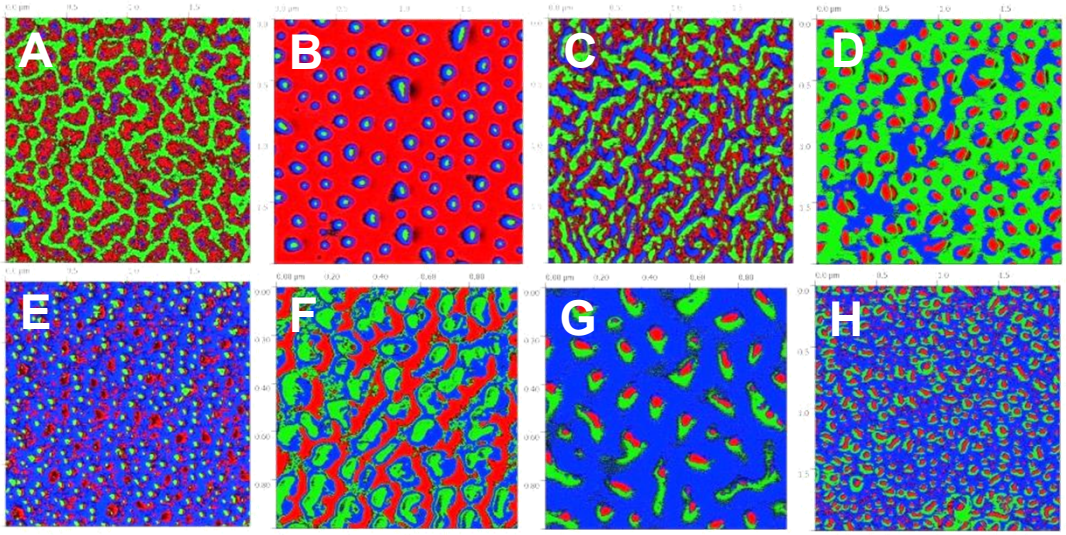
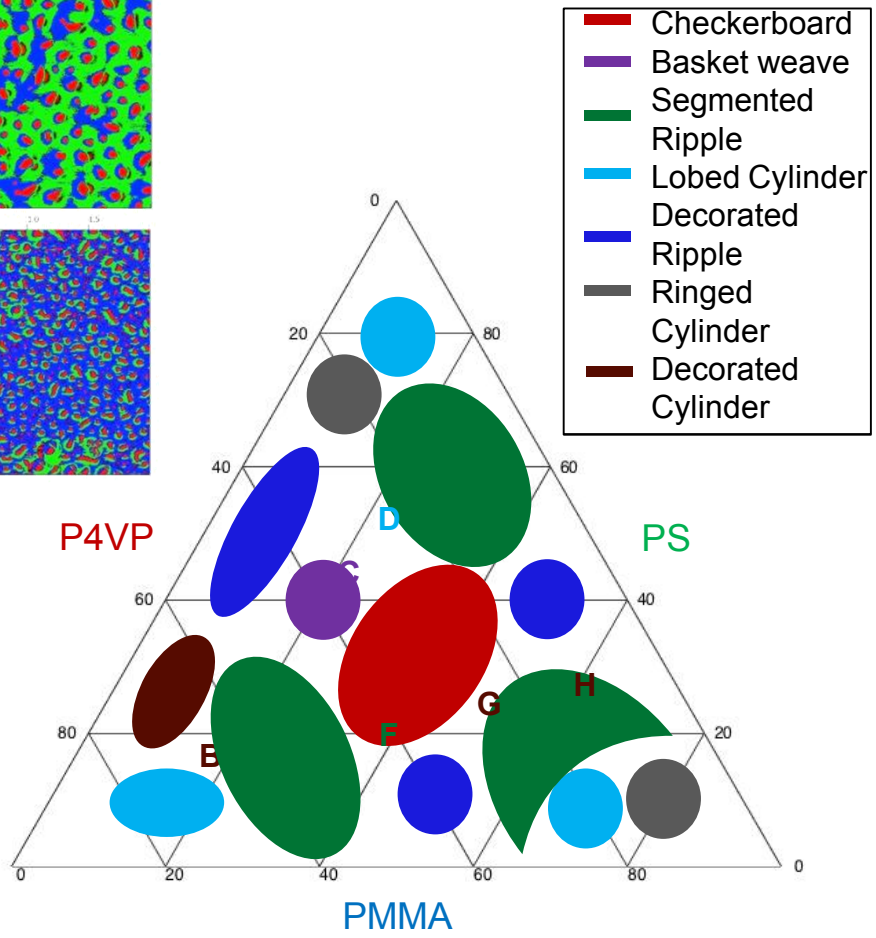
Matching Experiment to Theory





- Experimental phases match well with the simulated phases diagram
- Differences are caused by the difference in the χ values between the simulations and experiments

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Large cell SCFT compared to experiment

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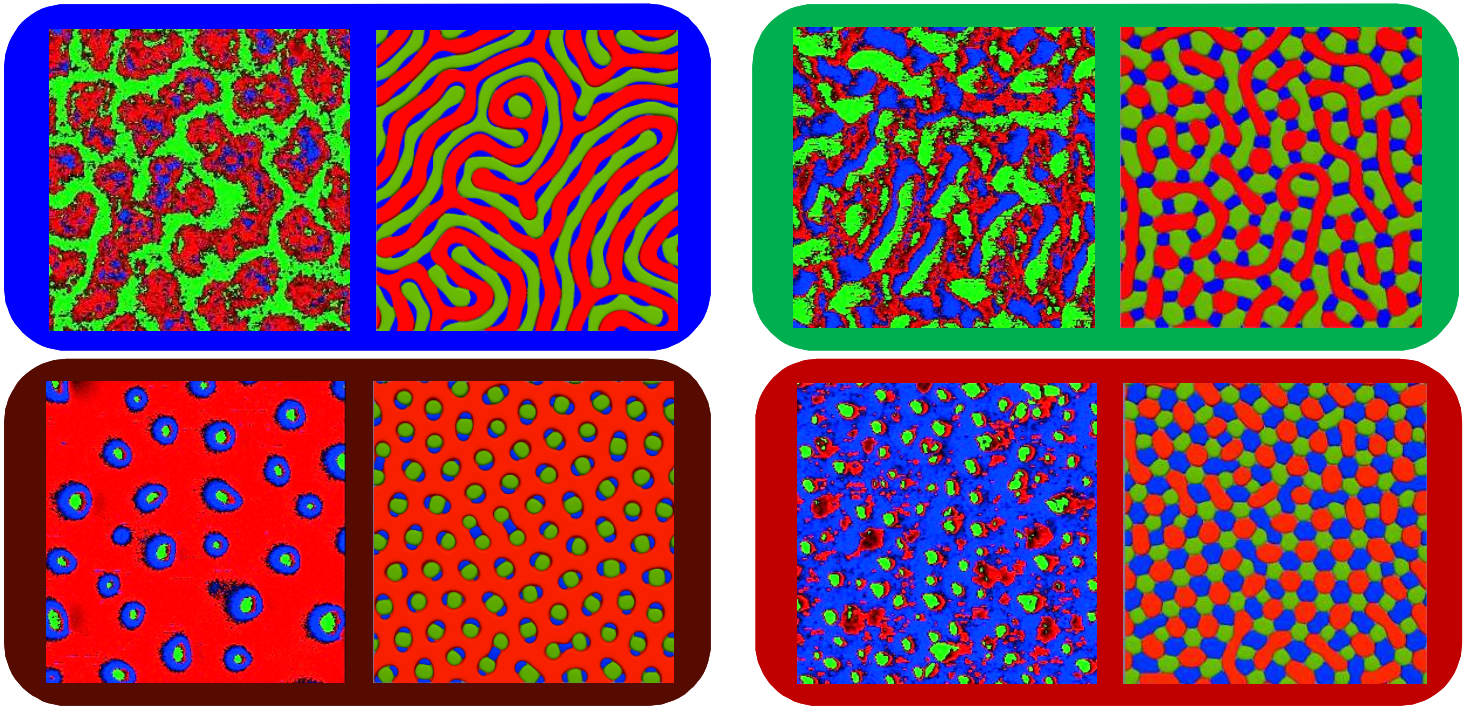
experimental images 1x1 μm
simulation images 50x50 R_g

qualitative agreement
no grafting density fluctuations in SCF



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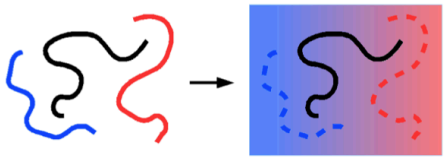
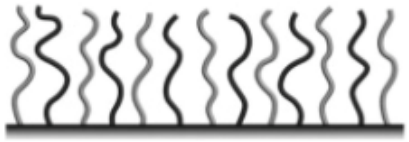
Rest of the Talk

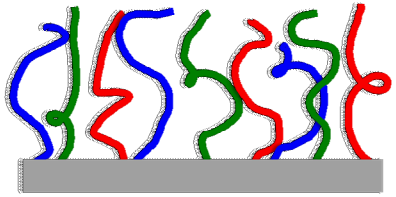
- polymer field theory



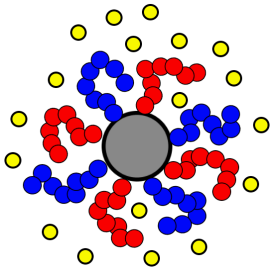
- binary brushes



- ternary brushes

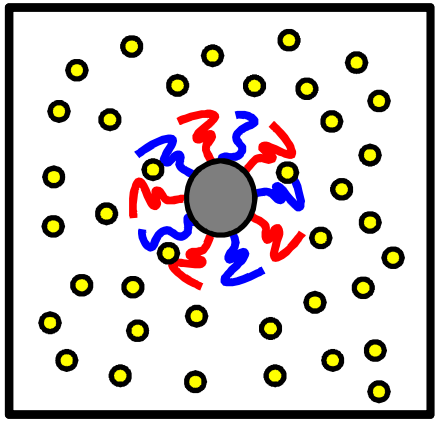


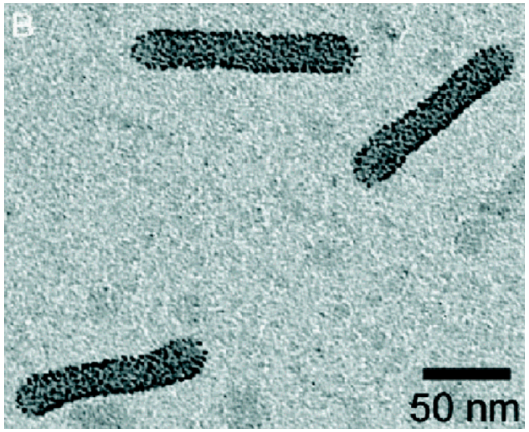
- binary brushes on nanoparticles



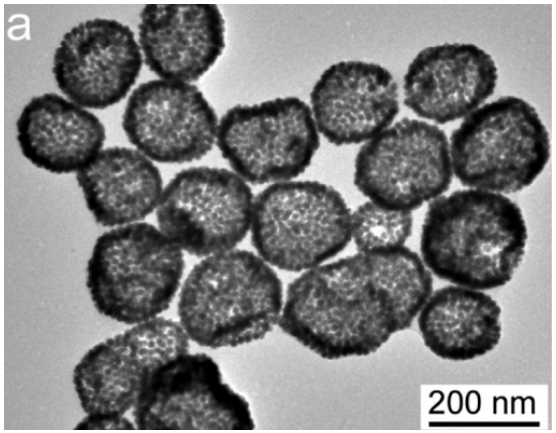
theme: effects of fluctuations

Mixed Brush on Nanoparticle in Solvent





Zubarev, *et al.*, JACS, 2006



Song, *et al.*, JACS, 2012

what brush structure do we expect on 1 particle?

how will many particles assemble?

SCF Brush Profiles

assume: $N_A = N_B$

$f_A = f_B$

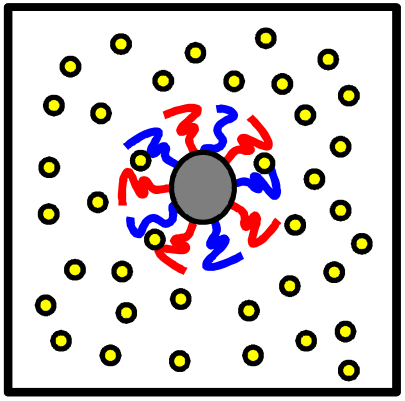
$\chi_{AS} = \chi_{BS} = \chi_S$

to compare to experiment

N = 60 kg/mol

PS-PMMA at 100°C, $\chi N = 18.9$

$R_P = 4.4$ nm

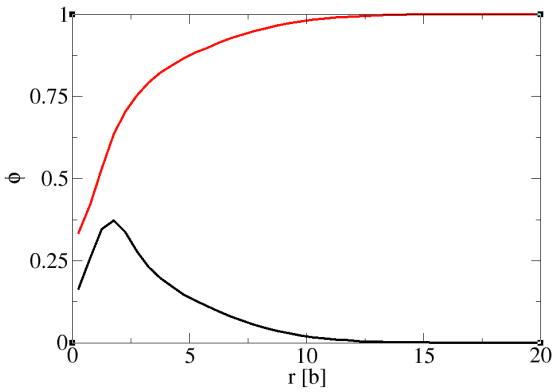


vary: R_P/R_g, σ, χ_{AB}, χ_S

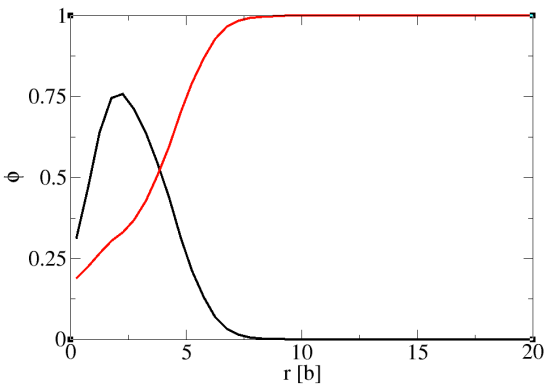
R_P = nanoparticle radius

$\chi_{AB}N = 28.3$

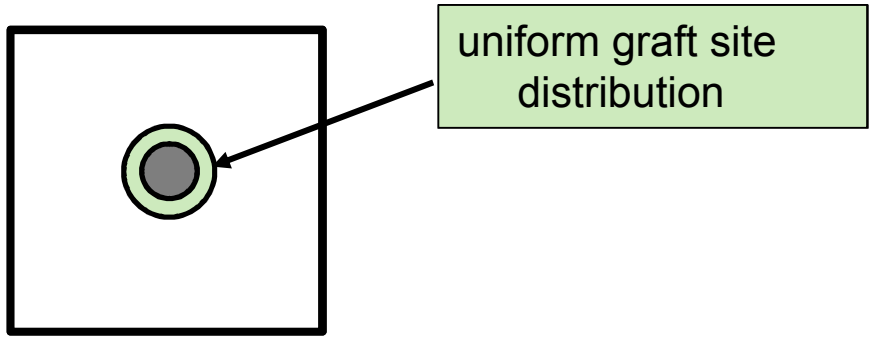
$\chi_S = 0.5$

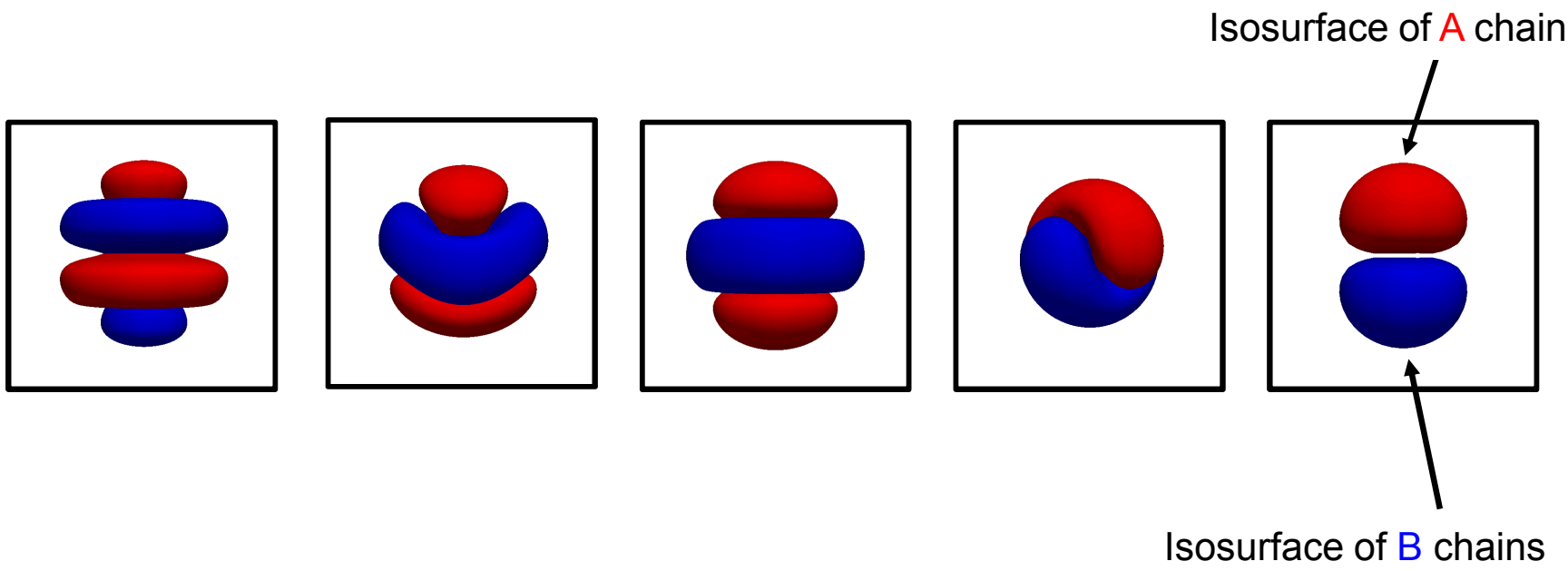


$\chi_S = 1.0$



Ordered Brush Isosurfaces from SCFT

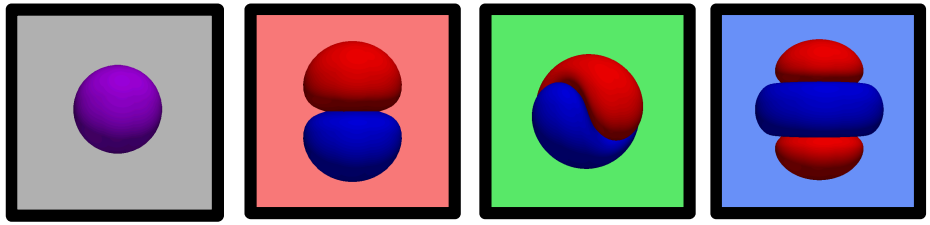




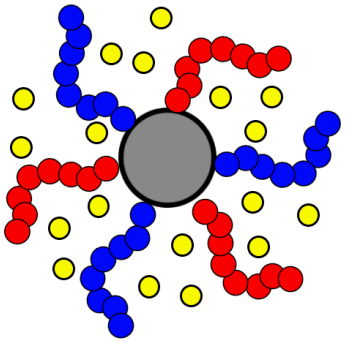
Effect of solvent quality

$\chi_{AB}N = 18.9$

$R_P = (2/3)R_g$

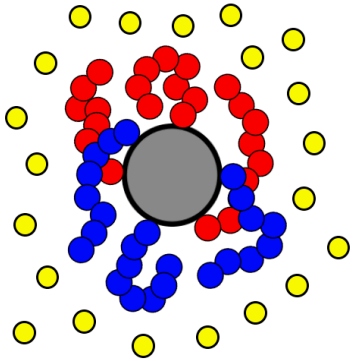


Low χ_S

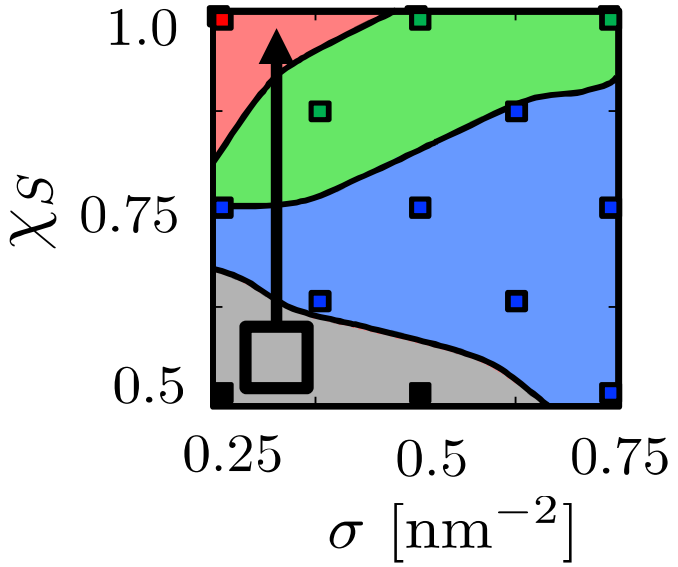


- High chain entropy
- Low enthalpy

High χ_S



- Low chain entropy
- High enthalpy

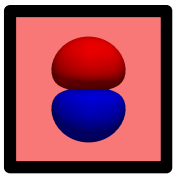


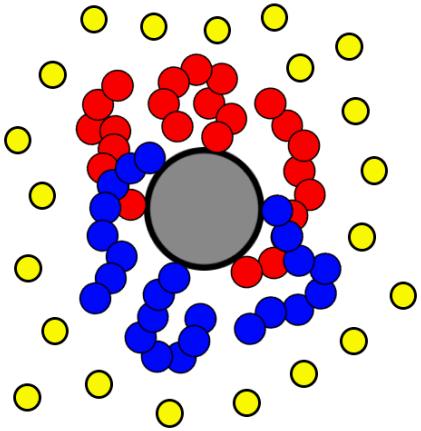
Effect of grafting density

$\chi_{AB}N = 18.9$

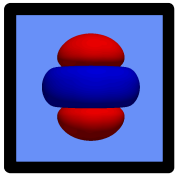
$R_P = (2/3)R_g$

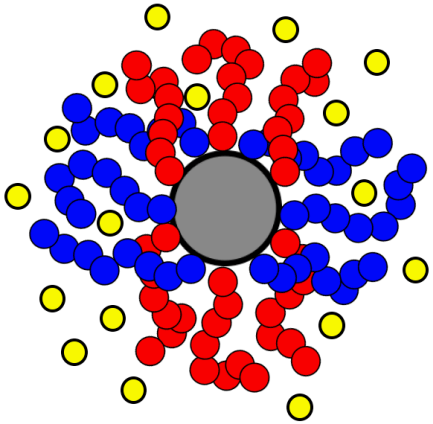
Low σ

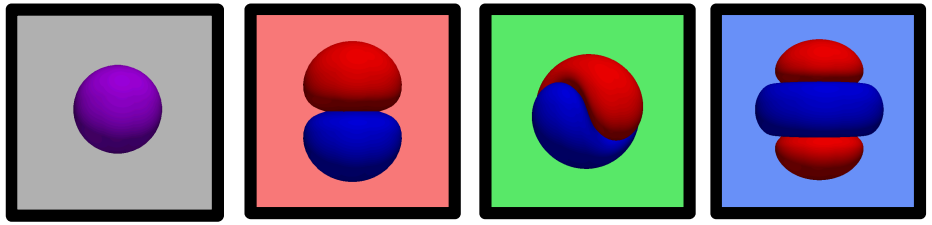


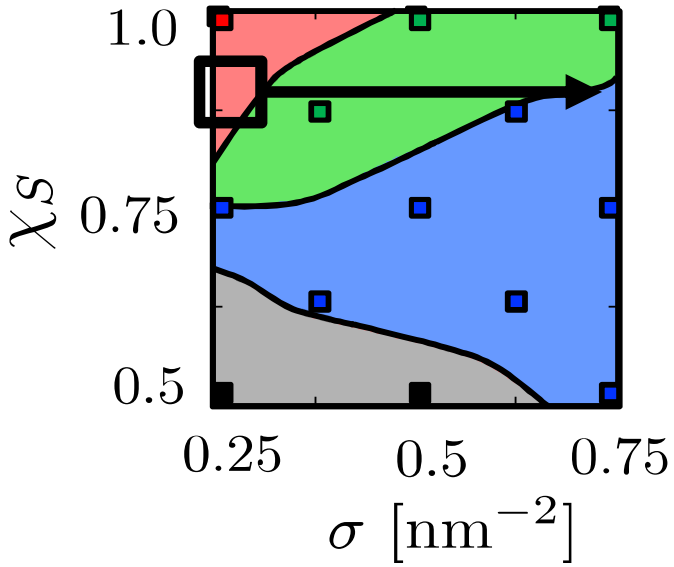


High σ



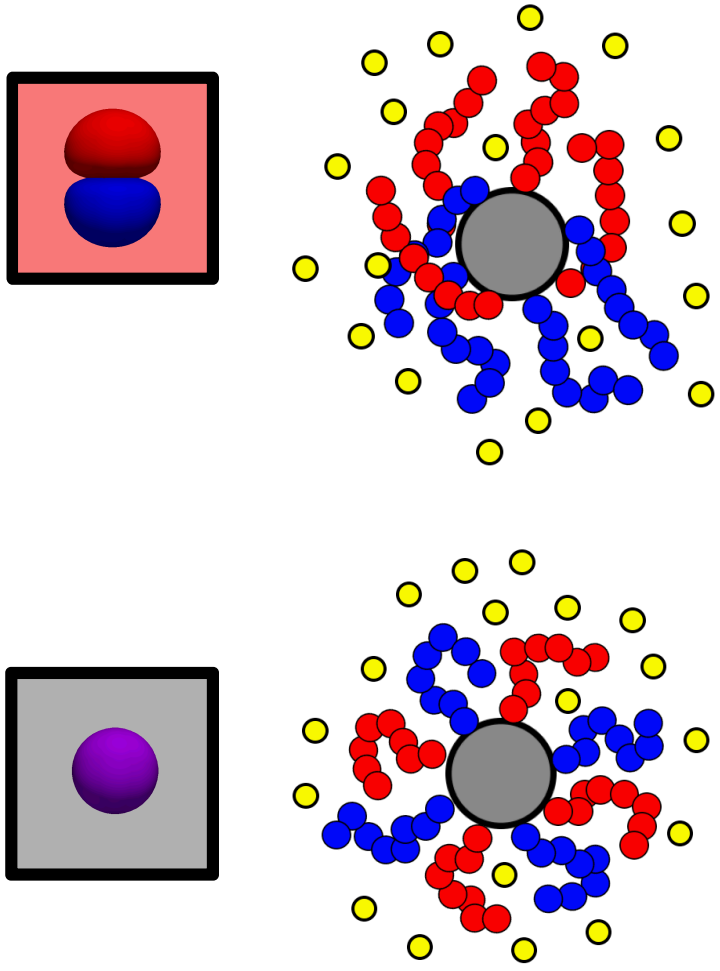


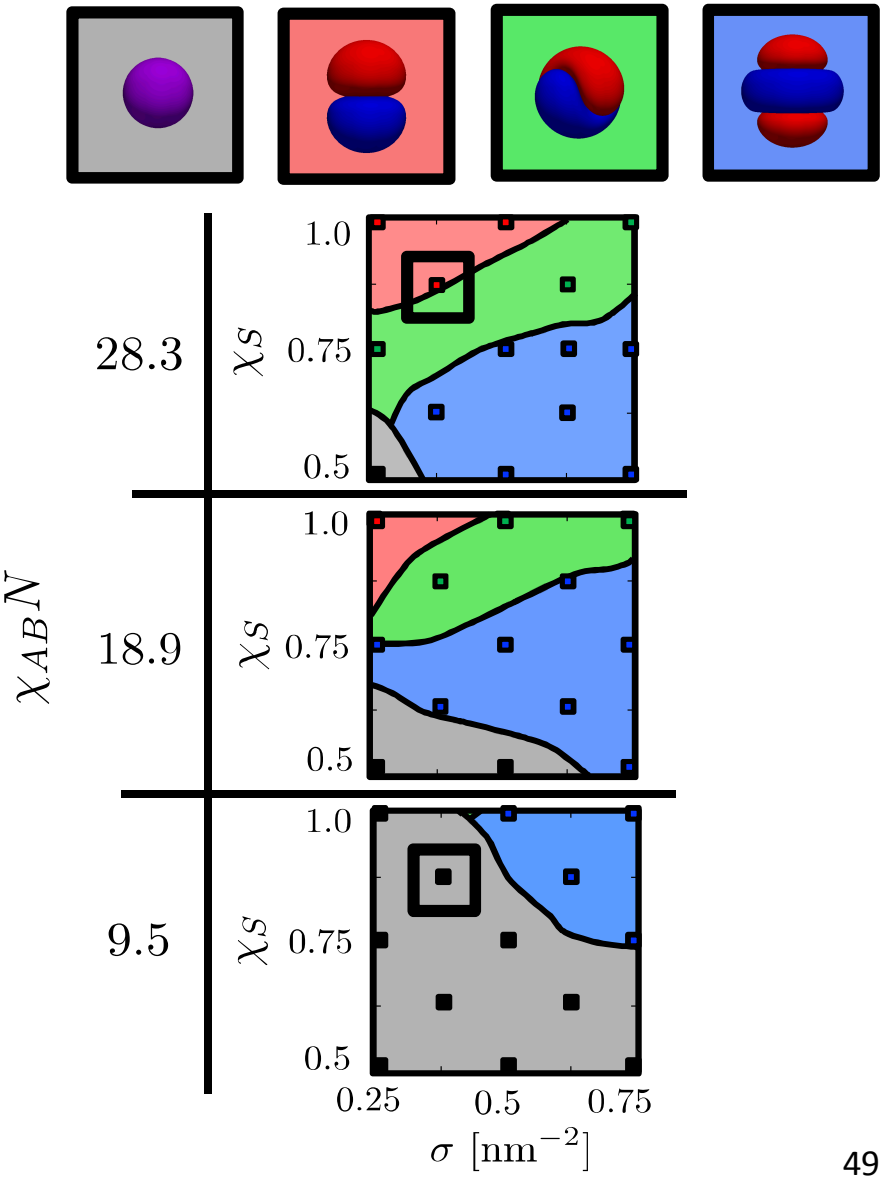




Effect of enthalpic repulsion

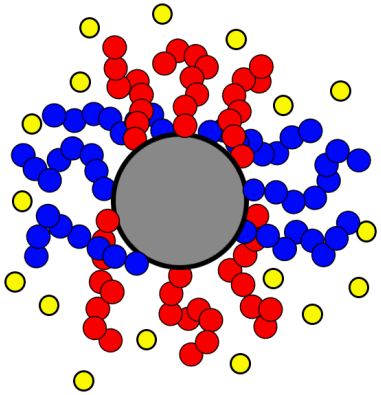
$R_P = (2/3)R_g$

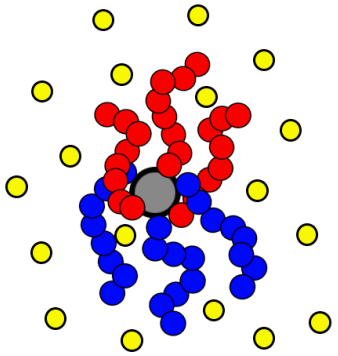


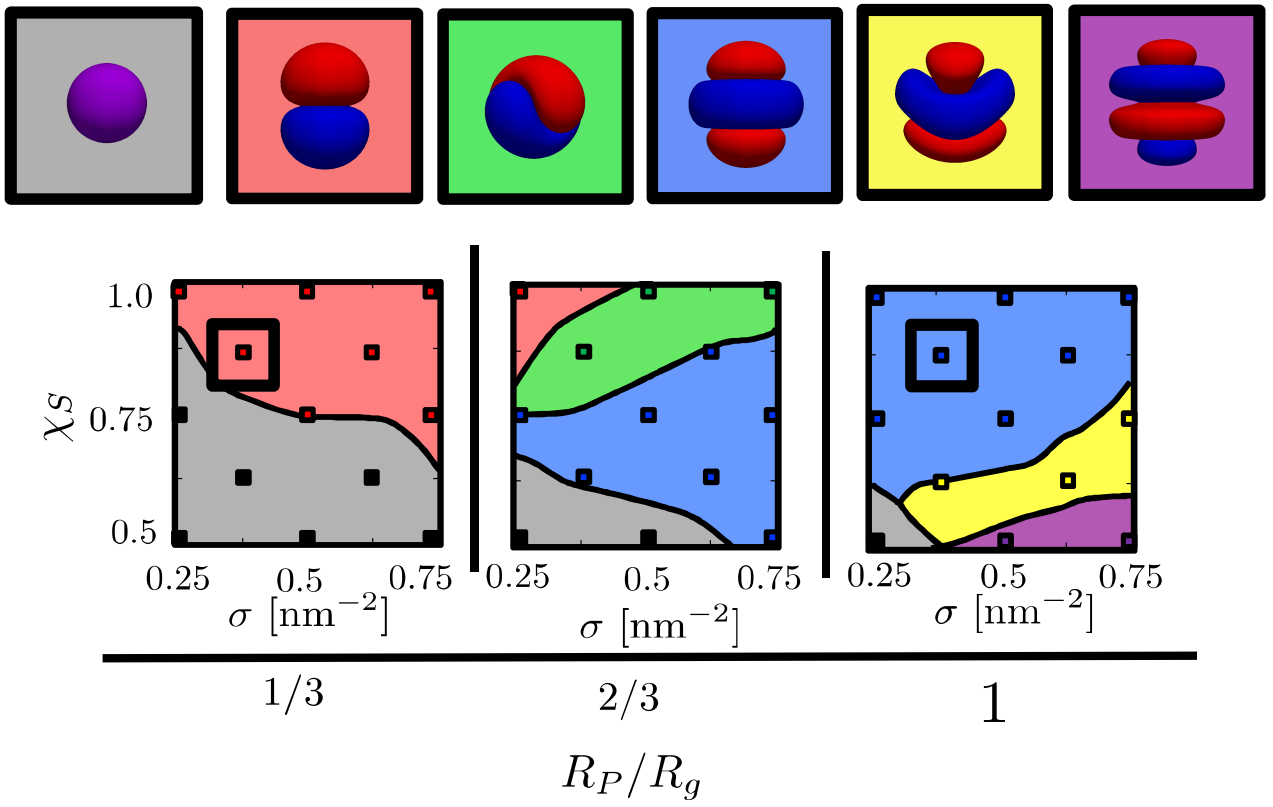


Effect of nanoparticle size

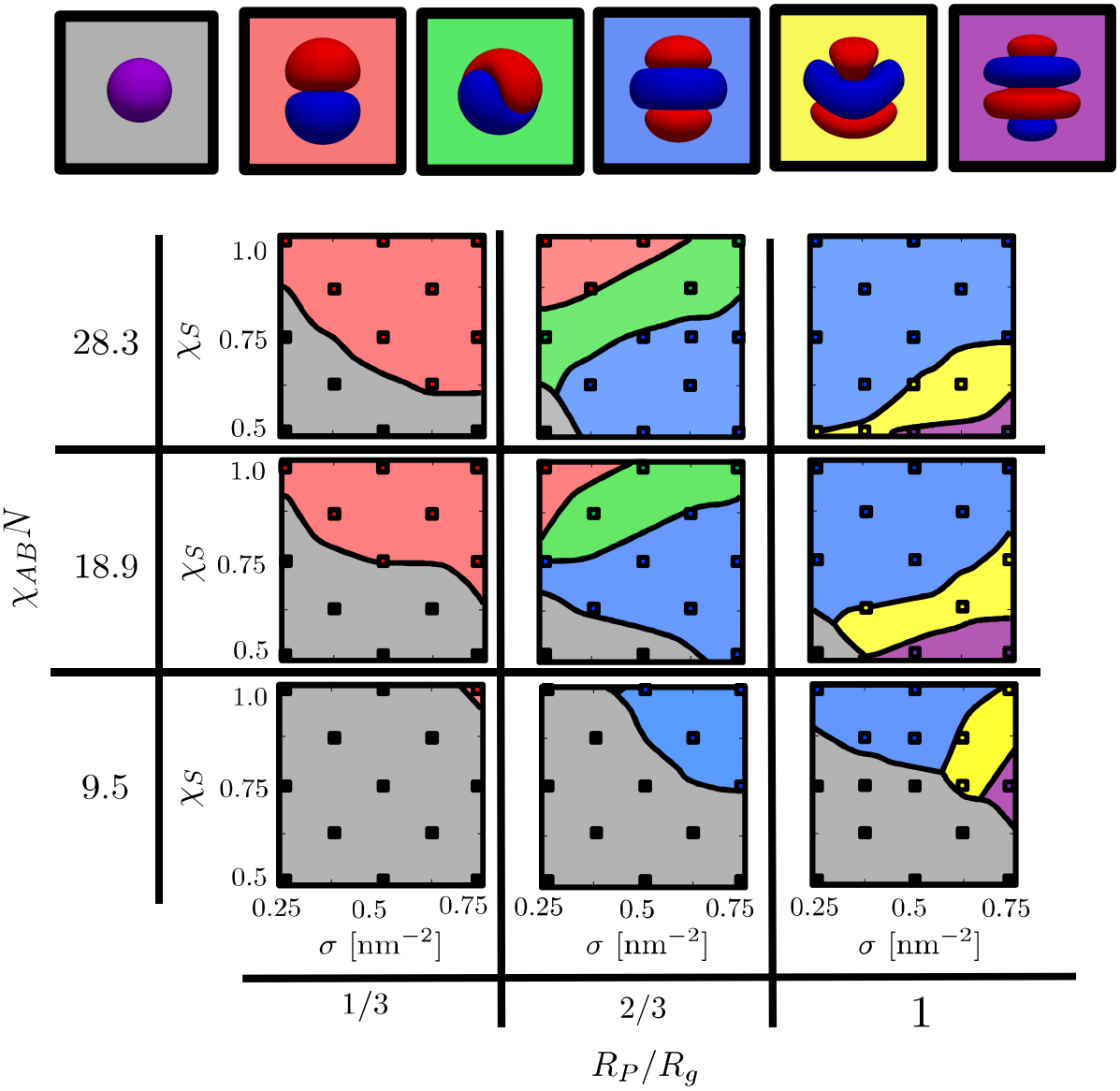
$\chi_{AB}N = 18.9$





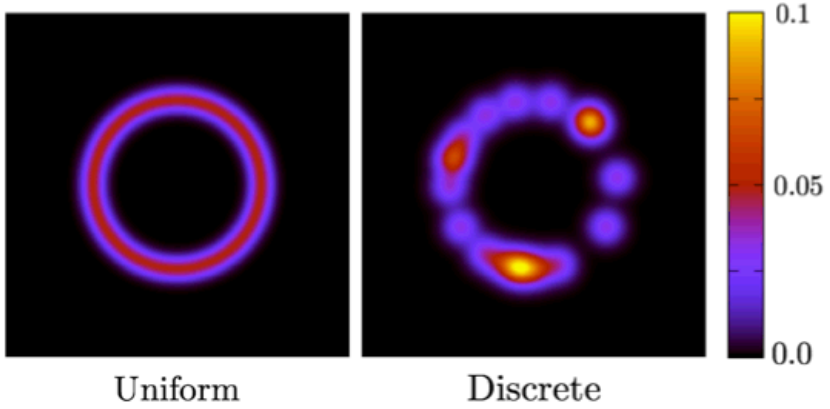


Full phase SCF diagram

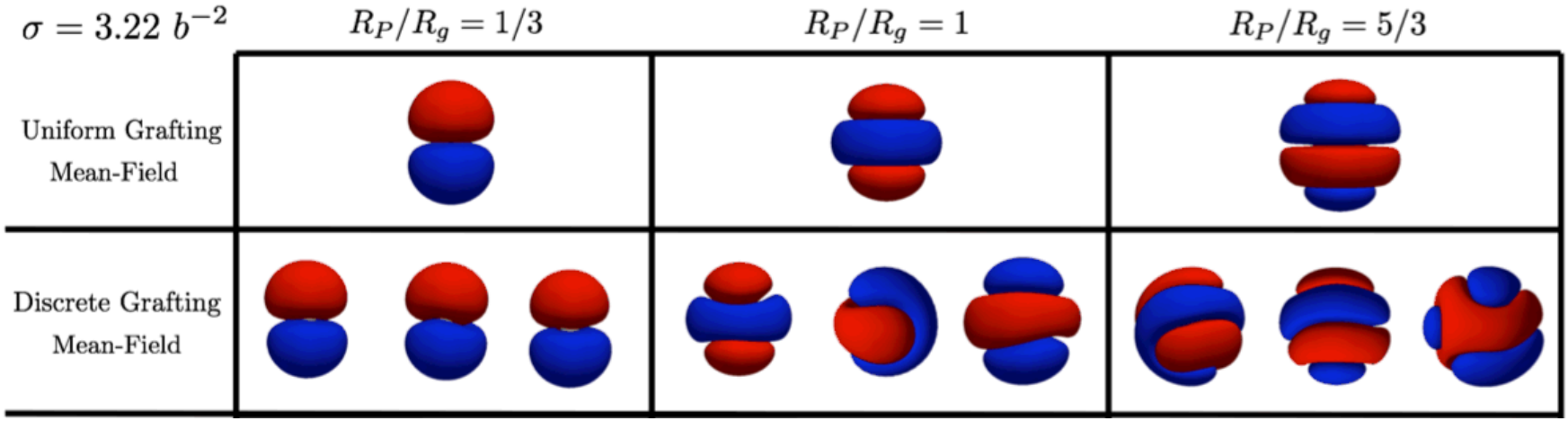


Fluctuation effects

uniform grafting is unlikely
allow discrete grafting



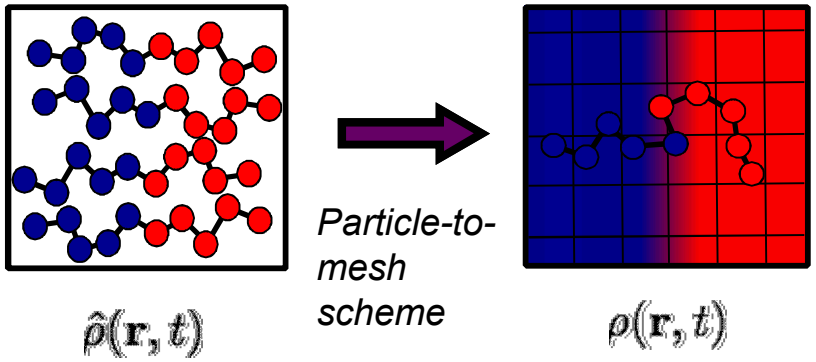
SCF structures less ordered



Dynamic Mean Field Theory

$$\mathcal{Z} = \prod_i^n \int \mathcal{D}r_i(t)$$

Rouse dynamics



Explicit access to particle positions

Efficient calculation of non-bonded forces

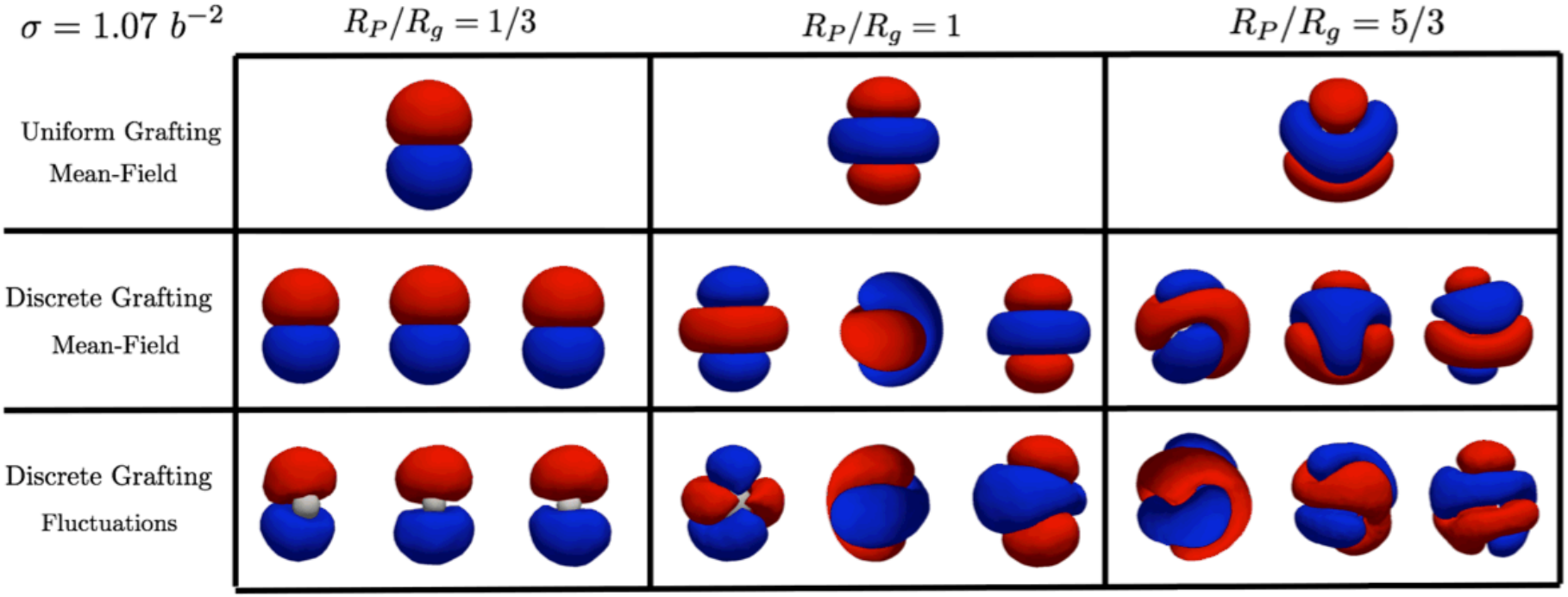
- Lose direct access to free energy
- Computationally expensive relative to SCFT
- Includes thermal fluctuations
- Includes randomness in grafting density

Fredrickson, Orland, *J. Chem. Phys.* 2014

Chao, Koski, Riggleman, *Soft Matter,* 2014

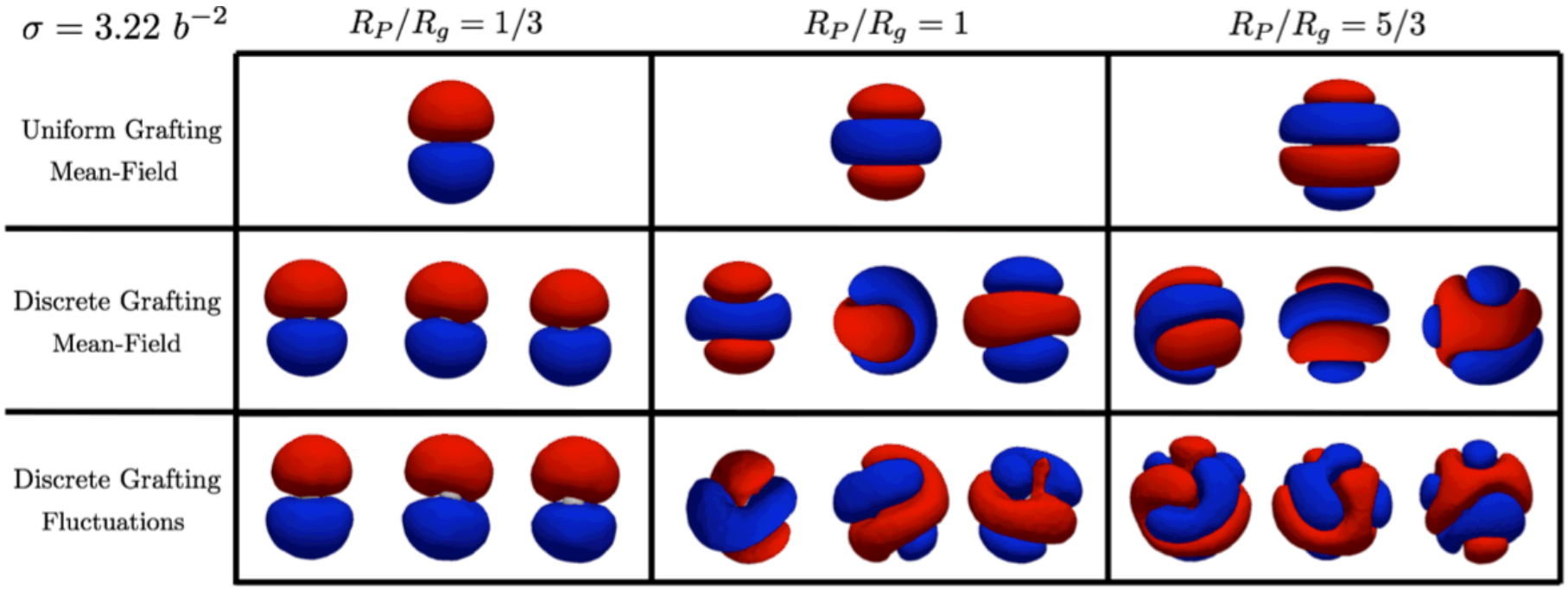
Thermal fluctuations

particularly important in solvent



Thermal fluctuations

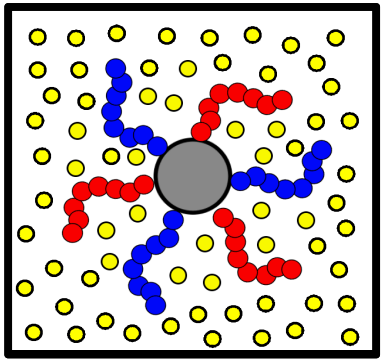
particularly important in solvent



prediction: Janus phase robust to fluctuations!

Koski and Frischknecht, in preparation

Mixed brush particle assembly



Yellow: Solvent
Red: “Hates Solvent”
Blue: “Loves Solvent”
Silver: Neutral Particle

DMFT calculations

80 nanoparticles in a box
$R_P = 2b$
$\sigma = 1 \text{ chain}/b^2$

Mixed brush assembly, $f = 0.5$

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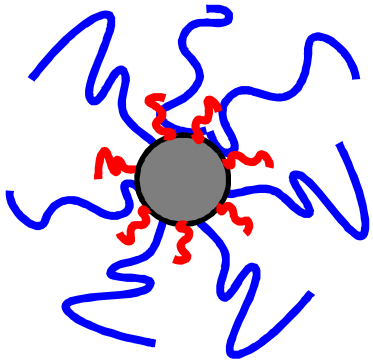
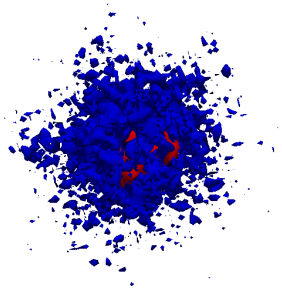
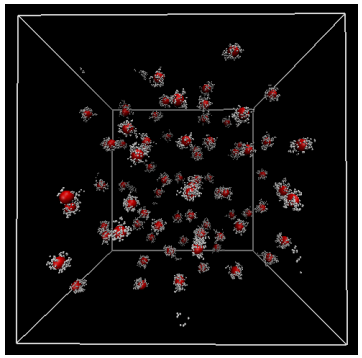
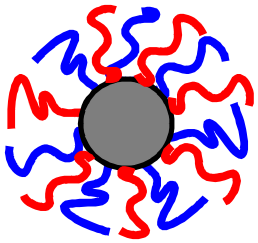
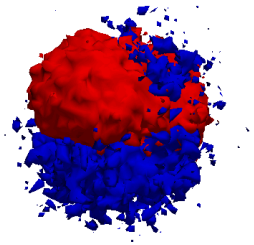
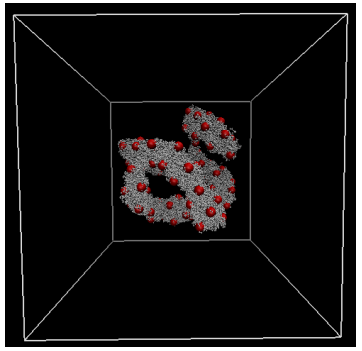
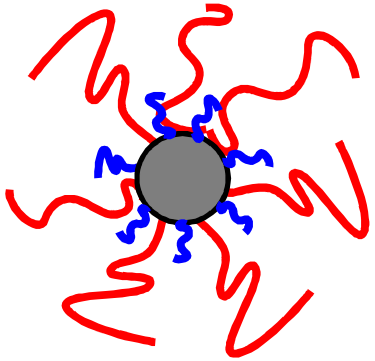
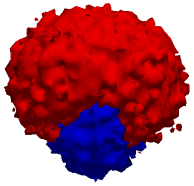
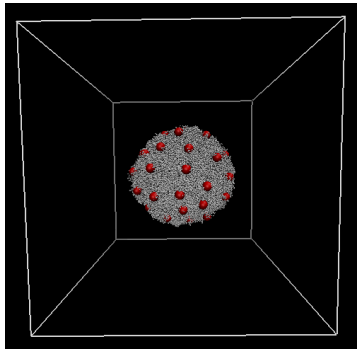
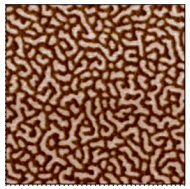
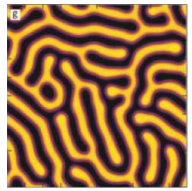
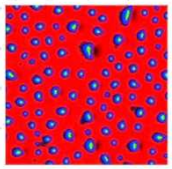
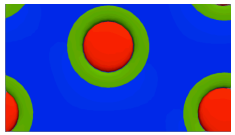
Long 'Loves Solvent' / Short 'Hates Solvent'			
Equal Size 'Loves Solvent' and 'Hates Solvent'			
Long 'Hates Solvent' / Short 'Loves Solvent'			

Conclusions

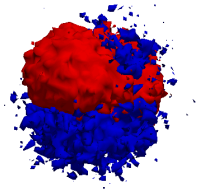
- binary melt brushes
  - SCFT phase diagram in good agreement with experiment
  - excellent lateral phase sep.
  - long-range order hindered by random grafting distributions

- ternary melt brushes
  - range of phase behavior with many laterally phase-separated patterns
  - all phase behaviors observed experimentally were observed in simulations

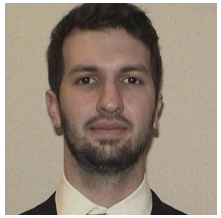
- mixed brush particles
  - Janus phase robust to fluctuations
  - interesting self-assembly



often must include fluctuations in modeling!

Acknowledgments



Dale Huber, Andrew Price, Chet Simocko, Jason Koski
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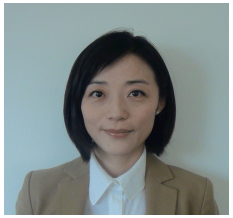


Glenn Fredrickson, Su-Mi Hur
UC Santa Barbara

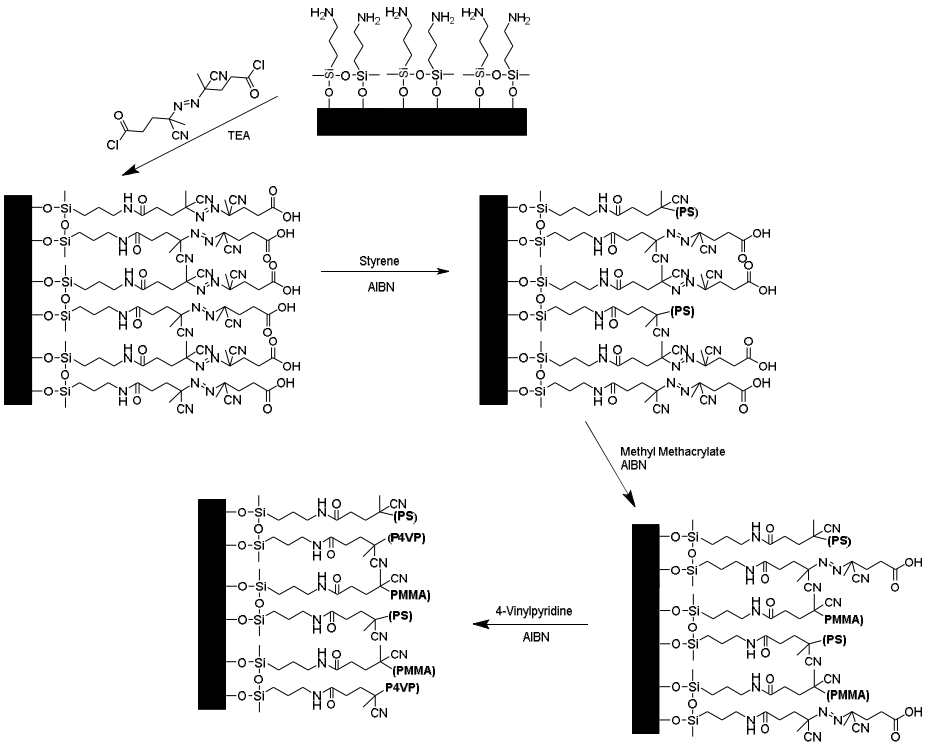

Rob Riggleman, Russ Composto
U Penn

Funding: LDRD, CINT, DOE-BES

Backup

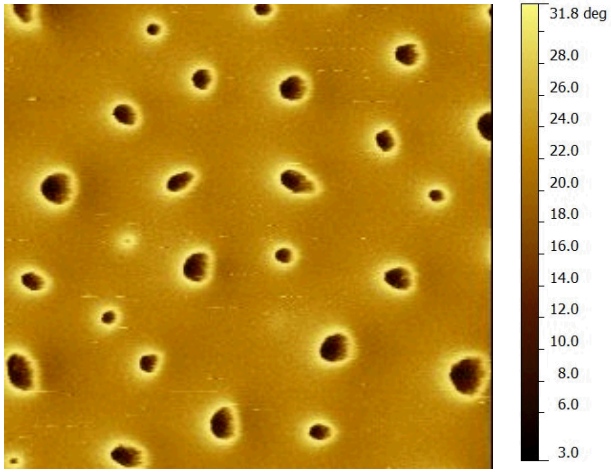
Sandia National Laboratories

Surface Initiated Growth



M_n: 56 – 130 kDa
brush thicknesses: 2.6 – 6 R_g
grafting density: 0.14 – 0.44 chains/nm^2

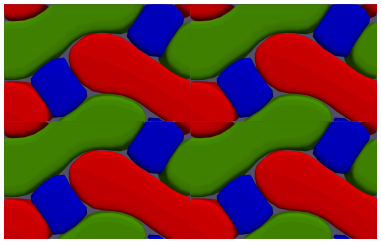
AFM phase contrast

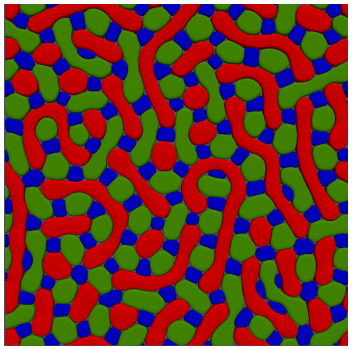


Chester Simocko, Amalie L. Frischnecht, Dale L. Huber. *ACS Macro Letters*, 2016, *5*, 149-153

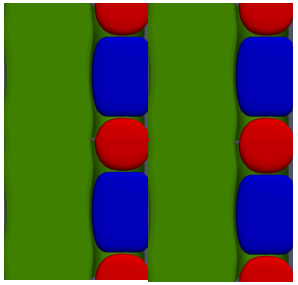
Results from fast quenches

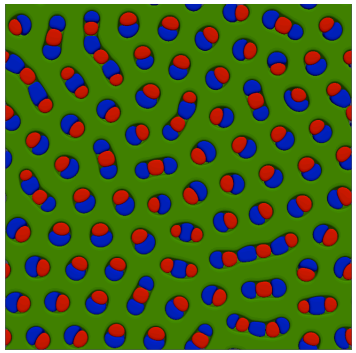
basketweave



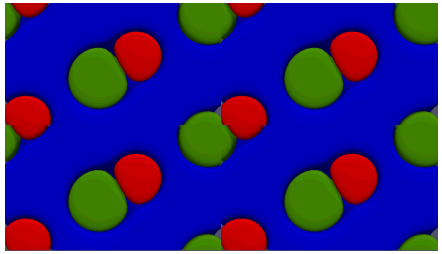


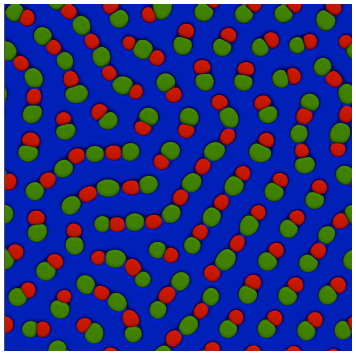
segmented ripple



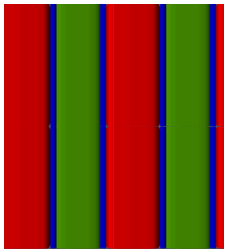


lobed cylinder



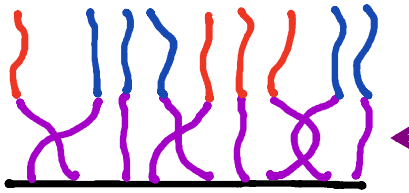


decorated ripple

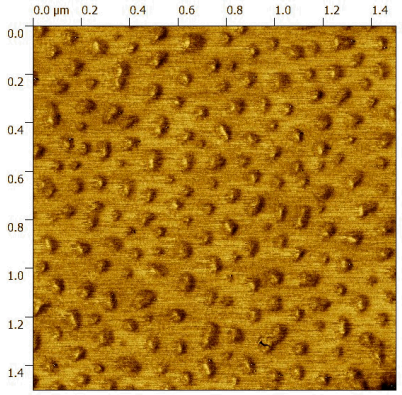


Summary of binary mixed brushes

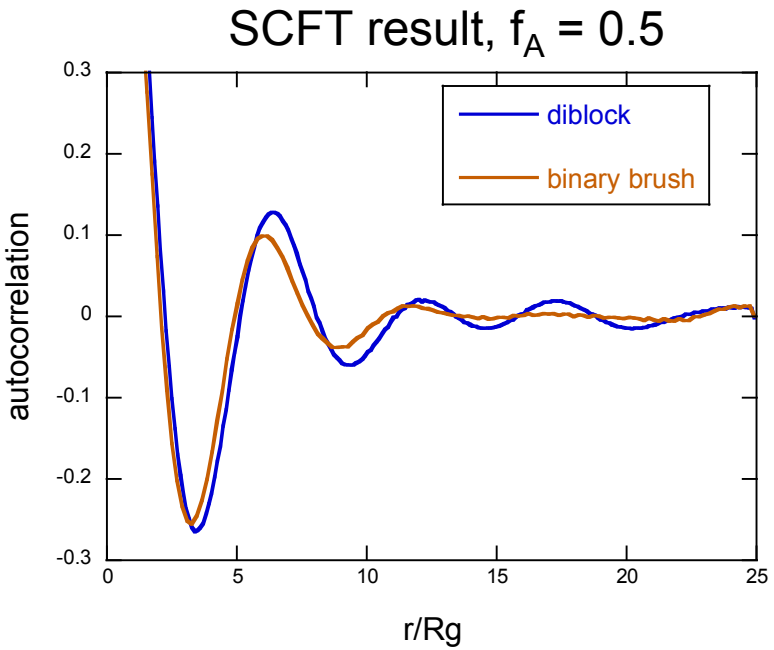
- in ideal case, directed assembly works for mixed brushes
- spatial variations in grafting prevent long-range order
- ideas for improved long-range order
  - better annealing methods for graphoepitaxy
  - random diblock copolymers to relax grafting correlations



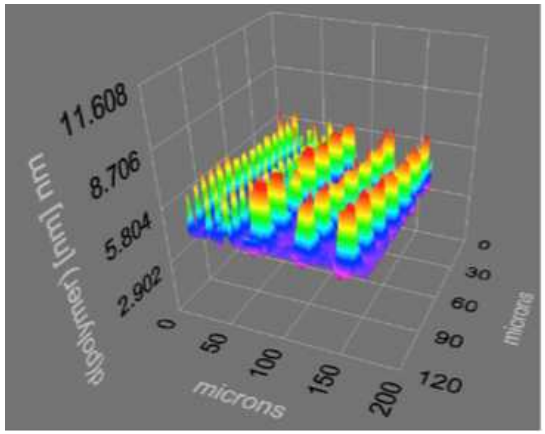
random PS-PMMA



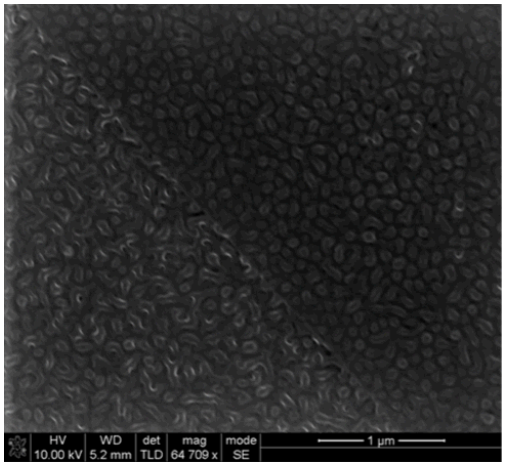
12% PS-
88% PMMA



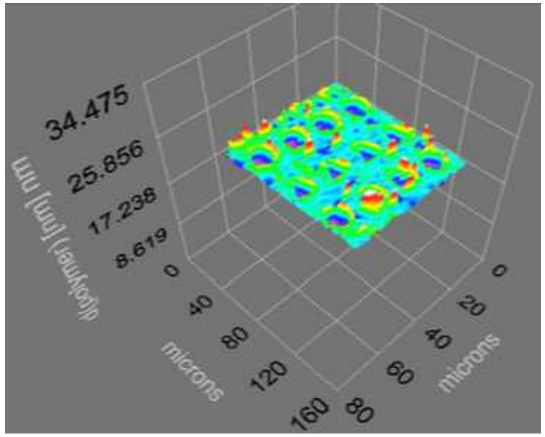
DSA attempts



patterned PMMA brushes



55%PMMA-45%PS next to
75% PMMA-25%PS



mixed PMMA-PS brushes

"pure" region is ≈ 15%
PMMA due to chain transfer

Huber, Price, and Frischknecht, SAND2010-7243 (2010).

Line Edge Roughness in SCFT

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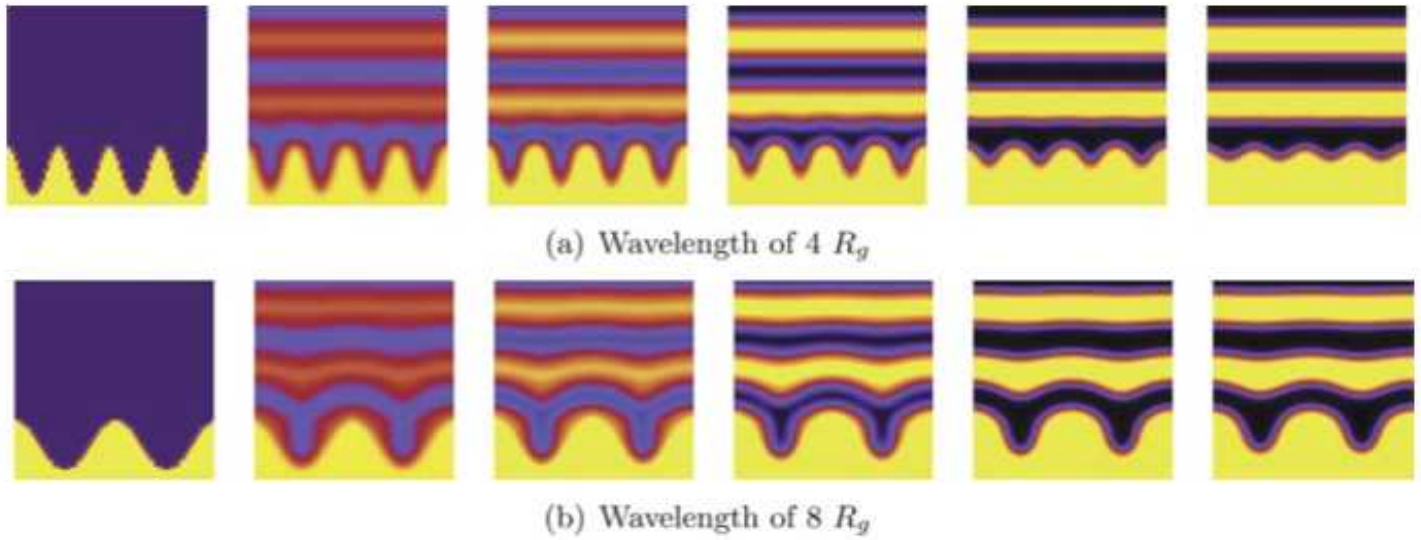
increasing brush height z



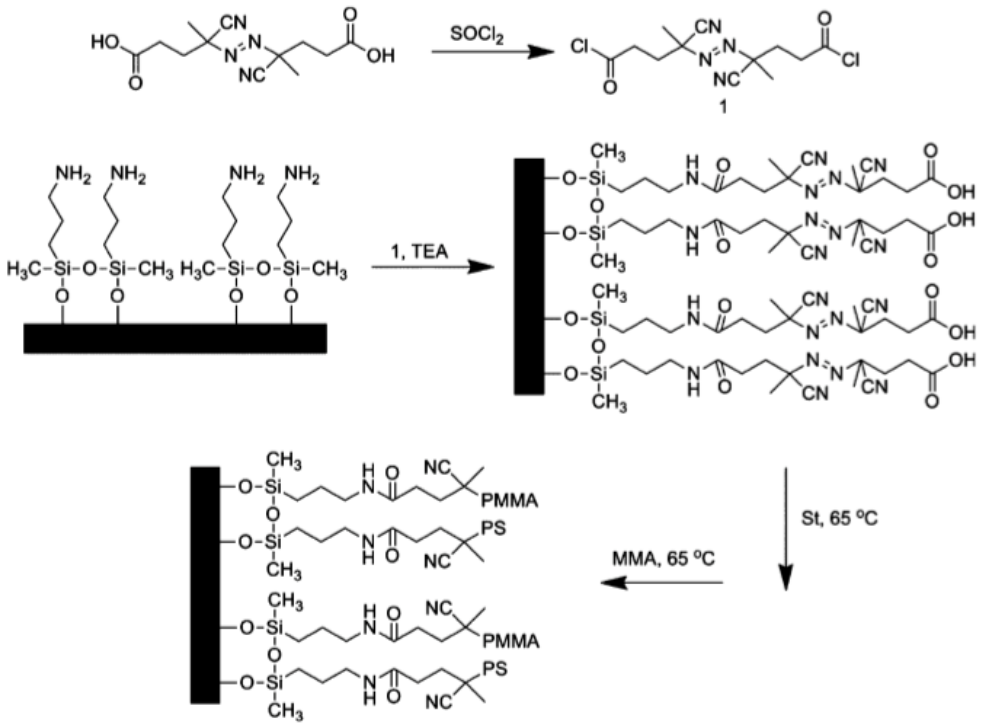
(a) Wavelength of 4 R_g

(b) Wavelength of 8 R_g

mixed brush maintains long-range order
better than block copolymer films

S. M. Hur, A. L. Frischknecht, D. L. Huber, and G. H. Fredrickson, *Soft Matter* **7**, 8776 (2011)

Synthesis of Mixed Brushes

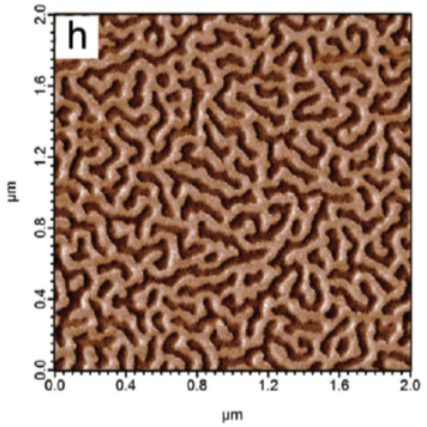


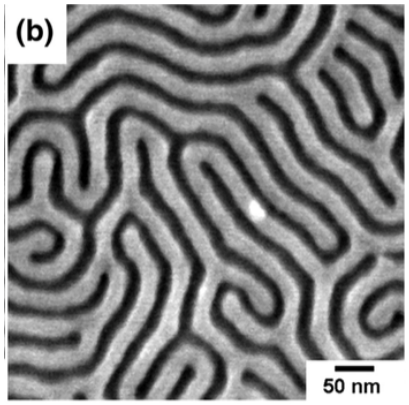
Mixed Brushes for Lithography?

mixed brush

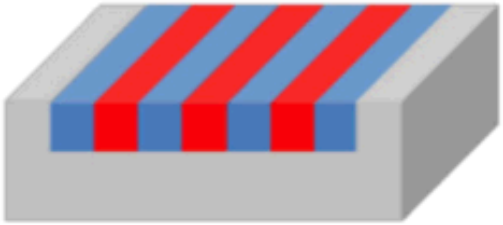
block copolymer

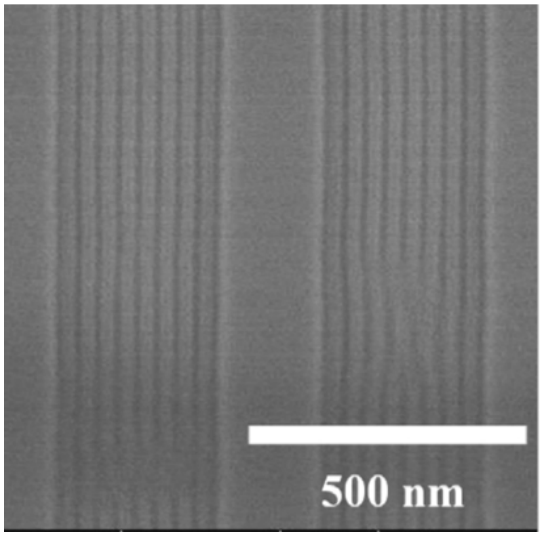
lateral phase separation
in PS-PMMA





alignment by graphoepitaxy in
block copolymer thin films





Morris, M. A. Microelectronic Engineering. *Microelectronic Engineering* **132,** 207–217 (2015).

Mixed brushes vs BCP thin films

Sandia National Laboratories

- block copolymer thin films
  - advantages
    - 25+ years of research and development
    - use beginning in semiconductor industry for lines, vias (hole shrink)
  - disadvantages
    - spin-casting limited to planar surfaces
    - difficult to turn sharp corners, make square patterns
- polymer brushes
  - advantages
    - could be made on any substrate, i.e. non-planar
    - chip-relevant architectures (e.g. 90 degree turns)
    - multiple patterns on same chip
    - potentially cheaper synthesis than BCP's; fast annealing
  - disadvantages
    - research still at early stages
    - more defects

Nanolithography using Directed Self-Assembly

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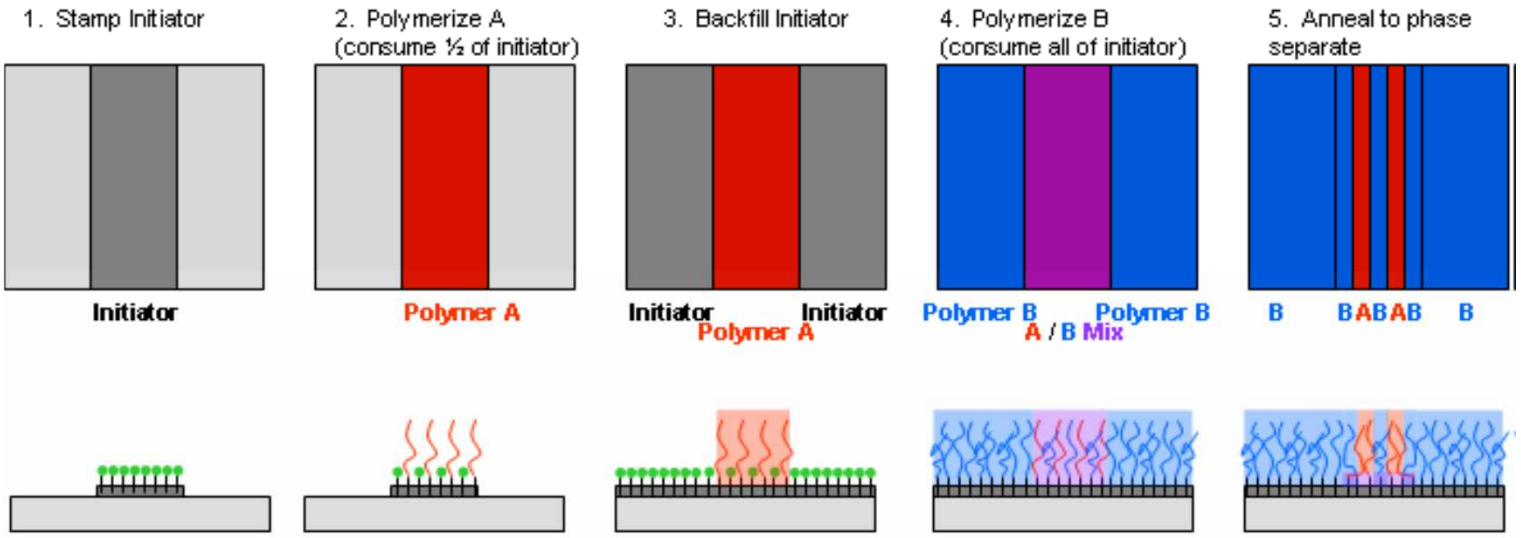
top view

side view



first: calculate phase diagram for melt mixed brush

D. L. Huber and A. Frischknecht. Nanopatterns by phase separation of patterned mixed polymer monolayers. US Patent 8652768 B1, February 18, 2014.

Does lithography idea work?

Sandia National Laboratories

bulk,
quenched

pure A region

patterned,
quenched

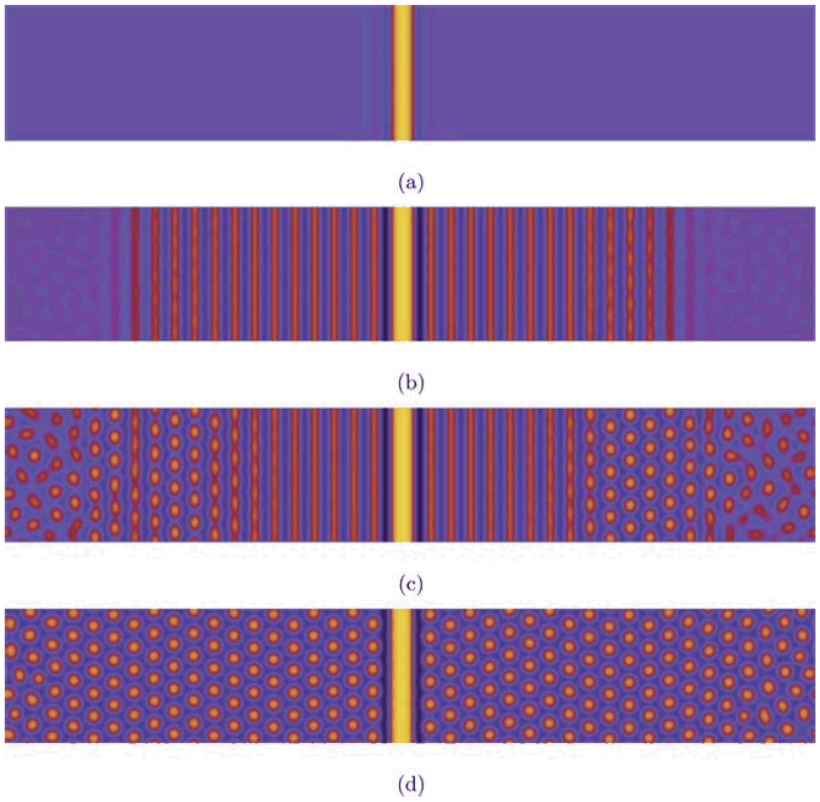
patterned,
slowly annealed

get long range ordered ripple phase in simulation

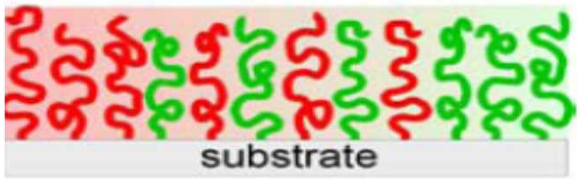
Hur, S.-M., Frischknecht, A. L., Huber, D. L. & Fredrickson, G. H.
Soft Matter **7,** 8776–8788 (2011).

Directed Assembly

aligned cylinder phase

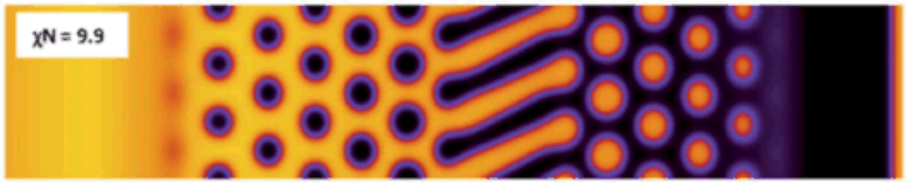


linear ramp in grafting density



A-rich domain B-rich domain

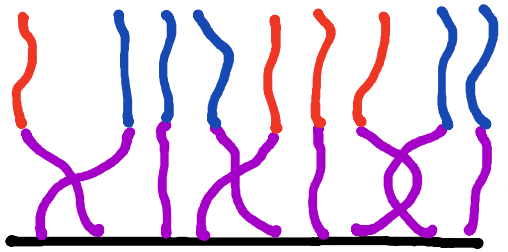
Increasing B homopolymer fraction



different shape features in one system

Improve order with diblocks?

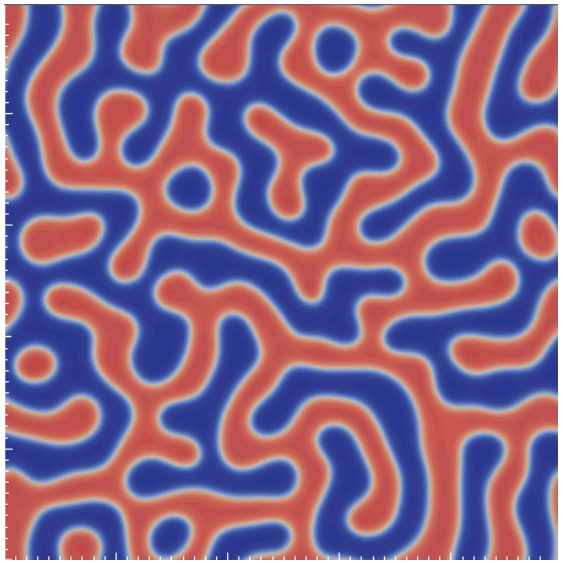
diblock mixed brush?

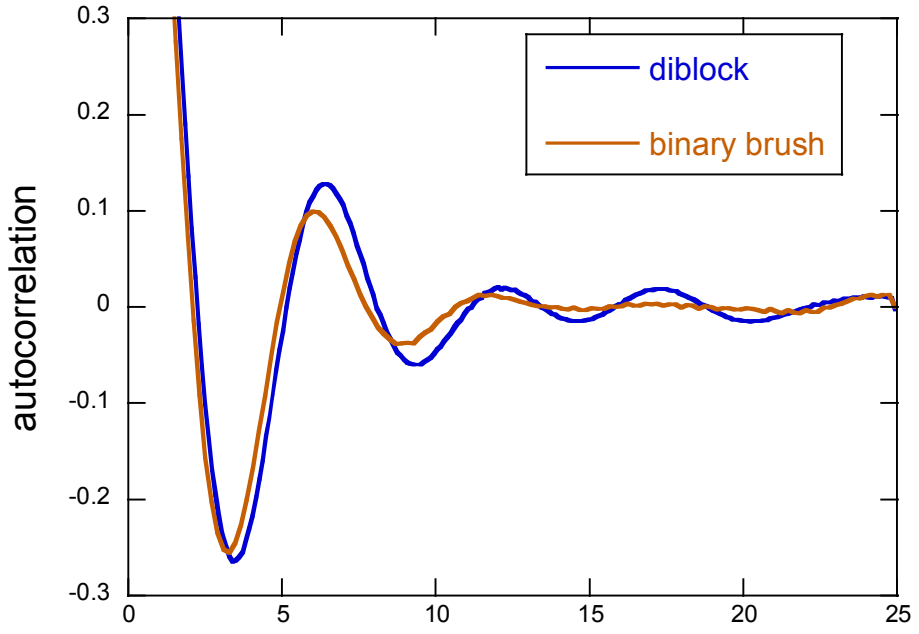


← random PS-PMMA

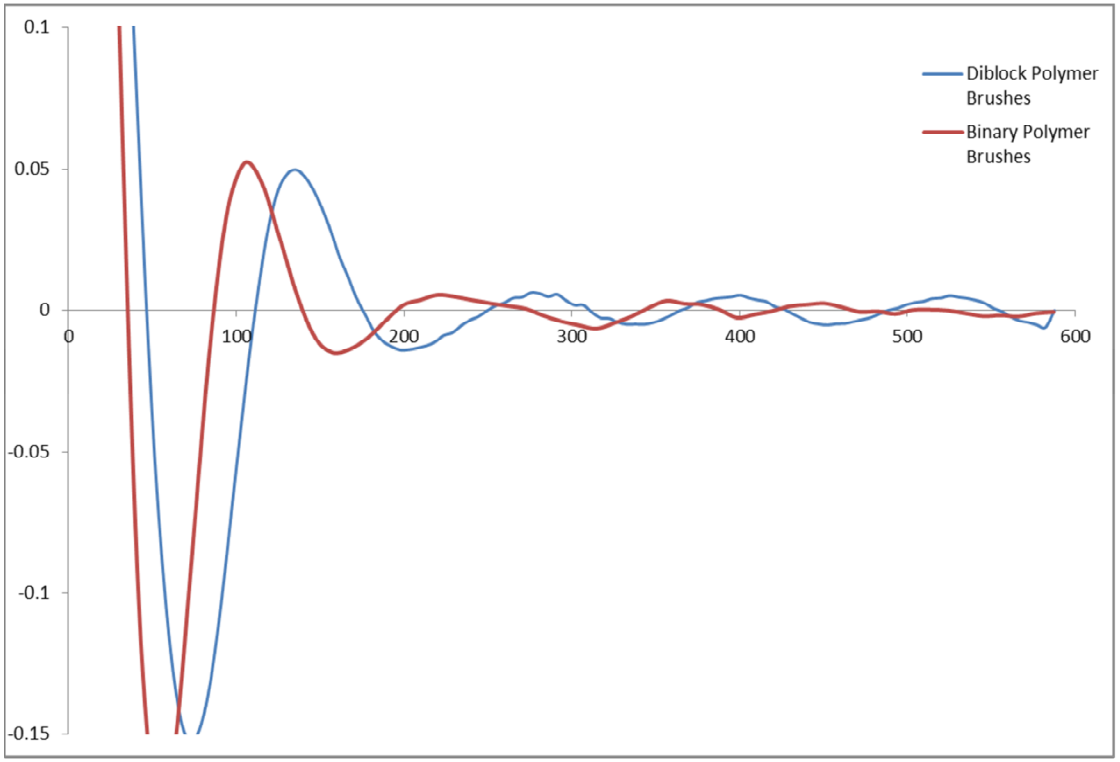
50% random copolymer, $f_{PS} = 0.5$

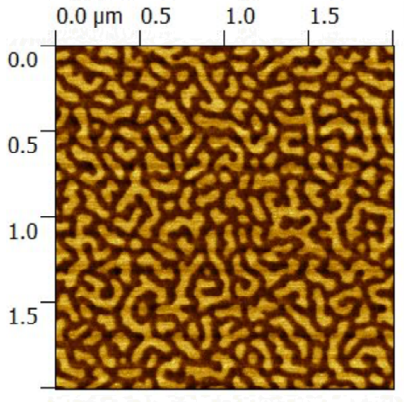
$\chi N = 16$ $\sigma = 0.5R_g$, $\Lambda^2 = 0.02$



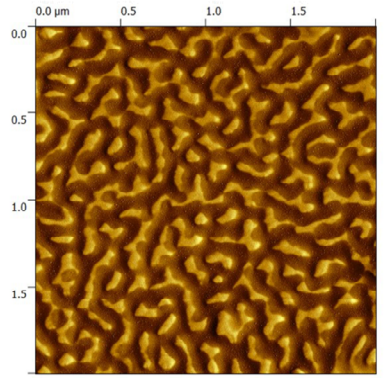


Experimental results





binary brush



diblock
binary brush

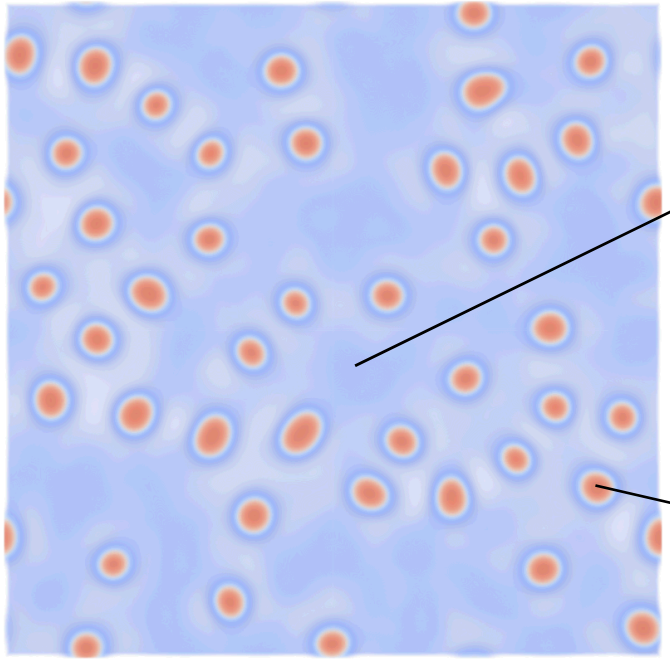
slightly more long range order

Diblock Mixed Brush

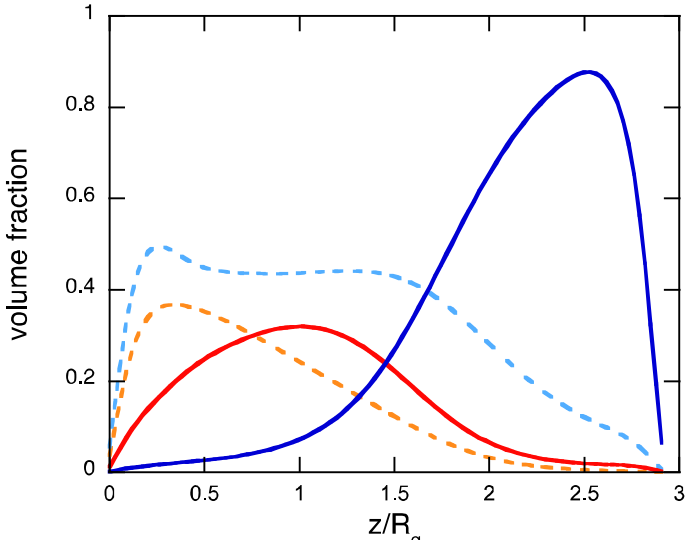
strong tendancy to vertically phase separate

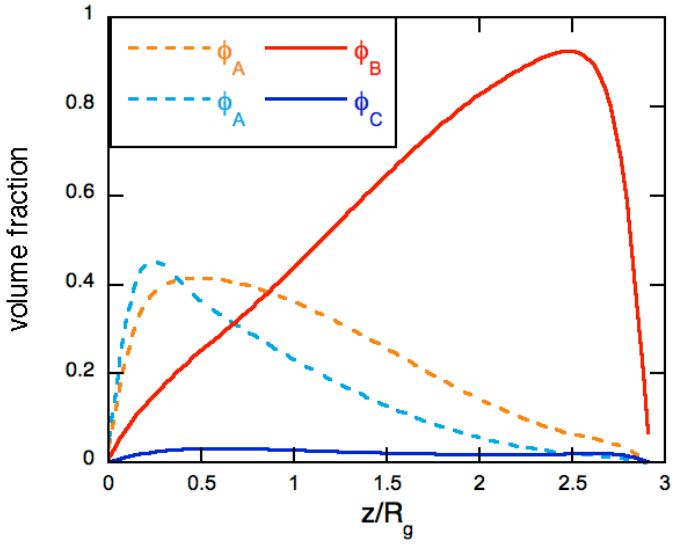
50% copolymer, $f_{PS} = 0.3$

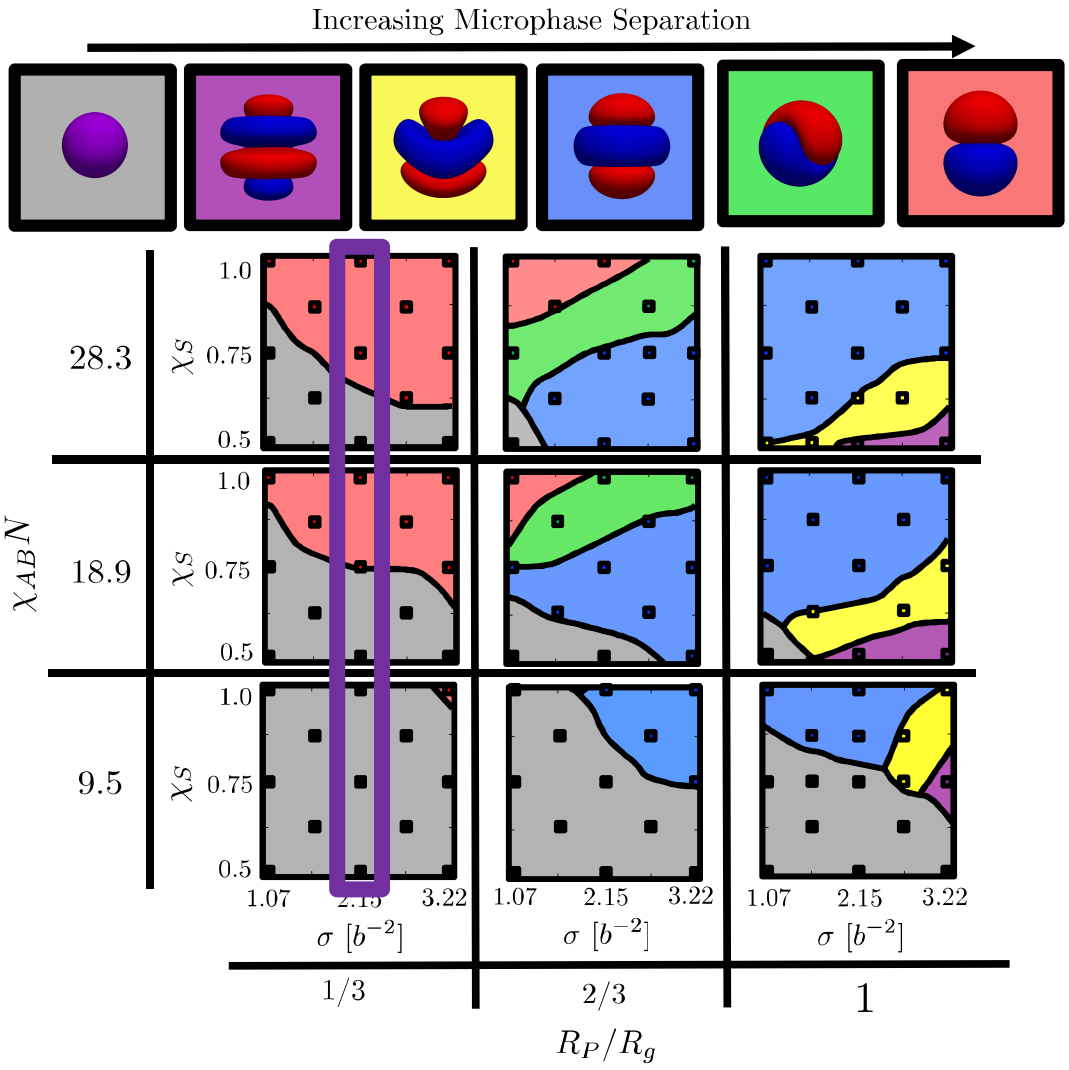
$\chi N = 16$



$\sigma = 0.5R_g$, $\Lambda^2 = 0.02$

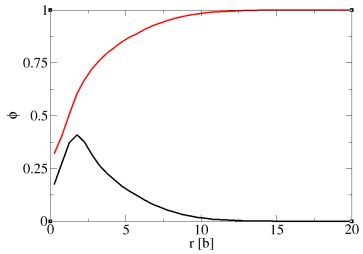
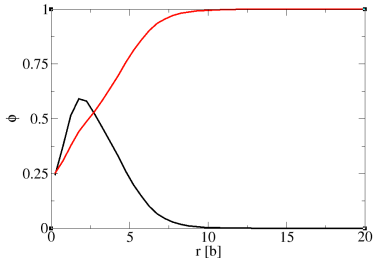
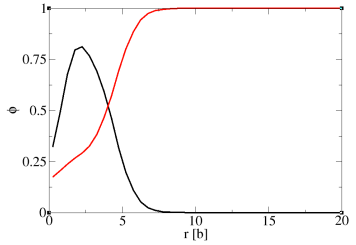
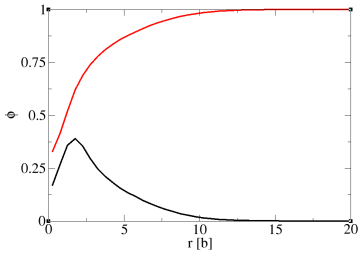
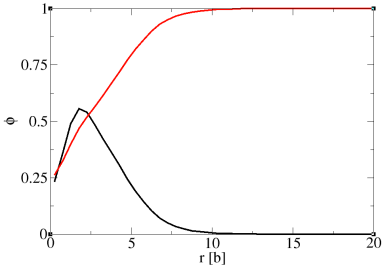
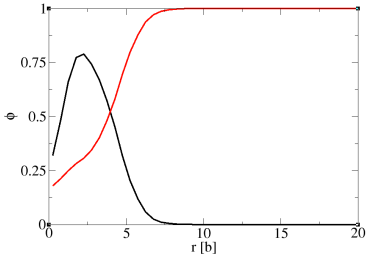





Increasing Microphase Separation
$\chi_{AB}N$
28.3
18.9
9.5
χ_S
1.0
0.75
0.5
1.07
2.15
3.22
$\sigma\ [b^{-2}]$
1/3
2/3
1
R_P/R_g

$\sigma = 2.15\ b^{-2}$

$R_P/R_g = 1/3$

	$\chi_S = 0.5$	$\chi_S = 0.75$	$\chi_S = 1.0$
$\chi_{AB}N = 9.5$			
$\chi_{AB}N = 18.9$			
$\chi_{AB}N = 28.3$